CHEMICAL ABSTRACTS

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1—APPARATUS

C. G. DERICK

Notice from the testing commission of the technical committee for chemical apparatus, section F. Laboratory apparatus. Supports. HERMANN RABE. *Z. Angew. Chem.* **34**, Aufsatzteil, 429–30(1921); 11 cuts.—*Supports with rectangular base.* Three sizes are proposed, the bases being 100 × 150, 130 × 230 and 150 × 300 mm., the corresponding rods being 500, 700 and 1000 mm. total length. Rods over 1000 mm. long, 16 mm. diam. are also approved. The diam. of the 500-mm. rod is 10 mm., that of the 700 and 1000-mm. rods is 13 mm., but the threaded end of all 3 is 10 mm. diam. The base is to be 15 mm. thick where the rod screws in, but may be lighter elsewhere, and the center of the hole is to be 25 mm. from the edge. It is in the end of the small sizes but may be either in the end or side of the large sizes. A foot 10 mm. diam. and 4–5 mm. high is at each corner. *Supports with tripod base.* The rods are the same as for the rectangular base, but the longest is 1000 mm. 2 types of base are proposed, plain and paw-foot, and 2 sizes for each type, the distances from the center of the hole to the tip of the foot being 95 and 115 mm. Cf. *C. A.* **15**, 2387.

J. H. MOORE

Practical laboratory apparatus. F. W. HORST. *Chem.-Ztg.* **45**, 795–6(1921).—*I. Siphon for drawing strong acid and alkali solns. from storage bottles.* The essential feature of the siphon is a small neck fused to the top of the bend. A stopper is inserted in the neck while the app. is operating, and it is quickly stopped by withdrawing the stopper. *II. Storage and emptying bottle for distd. H_2O.* A tubulure at the bottom of the bottle carries a stopper with a tube bent upward to the height of the neck and then a short bend to 1 side. The tube is lowered by turning in the stopper until the H_2O flows out.

J. H. MOORE

Preliminary balance for the analytical balance. A. PRANGE. *Chem.-Ztg.* **45**, 782(1921).—A brief description, with 1 cut, of a balance sensitive to 0.5 g. for finding wts. to the nearest g. before the final weighing on the analytical balance. J. H. MOORE

Small weighing beaker for the determination of the dry material in foods, etc. O. LÜNING. Brunswick. *Chem.-Ztg.* **45**, 831(1921).—This is a Ni beaker 60 mm. high and 50 mm. diam. The unusual depth reduces the danger of loss by spitting while drying.

J. H. MOORE

A new apparatus for the volumetric determination of phosphorus. BERTOLD MITAN. Charlottenburg. *Chem.-Ztg.* **45**, 796–7(1921).—The app. is designed especially for use in Fe and steel labs. It consists of 2 bottles, 1 for 0.5 *N* NaOH, the other for 0.5 *N* H_2SO_4, standing on a titration rack. Attached to the rack below the NaOH bottle is a pipet with an over-flow tip at the top, the NaOH soln. being delivered to the pipet through a side-tube near the bottom. The vol. of the pipet is such that it discharges just enough soln. to dissolve ammonium phosphomolybdate equiv. to 0.02 g. P. Below the H_2SO_4 bottle is a buret with an over-flow tip and a zero mark near the bottom, the vol. between zero and the over-flow being the same as that of the NaOH pipet. The buret is graduated upward in 400 equal divisions, the 20th division

being marked 0.1, the 40th marked 0.2, etc., which enables one to read the % P directly from the buret with an accuracy of 0.005%. To operate, the ammonium phosphomolybdate is pptd. from 1 g. of the sample in the usual way, washed and transferred with the filter to the titration flask, 1 pipet of the NaOH soln. added and a few drops of phenolphthalein soln. after the ppt. is dissolved. The excess NaOH is then titrated with the acid from a *full* buret and the % P read from the buret. The 0.5 *N* solns. are used for Fe high in P. For low P a similar app. with 0.2 *N* solns. is used, the NaOH pipet holding enough soln. to dissolve a ppt. equivalent to 0.005 g. P. The buret is divided into 200 divisions, the 10th being marked 0.01, the 20th marked 0.02, etc. 2.5 g. of the sample must be used, and the reading is accurate to 0.001% P. The app. is made by H. Göckel, Berlin. J. H. MOORE

Franke's hydrogen sulfide generator. HERMANN ZELLER. *Z. angew. Chem.* **34**, Aufsatzteil, 439(1921); 2 cuts.—The acid bottle, with a tubulure at the bottom, stands on a shelf above the bottle containing the FeS. The latter bottle has 2 tubulures at the bottom, 1 connecting with the acid bottle and the other carrying a cock for drawing off the spent acid. The H_2S passes from the top of this bottle through a washer to the pptg. flasks. J. H. MOORE

A simple gas generator. PAUL H. PRAUSNITZ. Jena. *Z. angew. chem.* **34**, Aufsatzteil, 434(1921).—The app. is similar to Franke's (preceding abst.) except that plain bottles with 2-hole stoppers are used, the siphon from the upper bottle reaching to the bottom of the lower bottle which is covered with broken glass to a depth of 3–5 cm. The substance (Zn) on the glass is protected from any acid not forced into the upper bottle when the exit cock is closed. J. H. MOORE

Return-cooler with countercurrent. F. MACH AND P. LEDERLE. Augustenburg. *Chem.-Ztg.* **45**, 779(1921).—The mantle of the cooler is open at both ends and has 2 nipples for attaching the H_2O connections fused on the same side a short distance from the ends. The condensing tube is held in by stoppers in each end of the mantle which is divided into 4 or more cells by slipping disks of cork or rubber of suitable size on the tube. The cold H_2O enters near the bottom of the top cell and each disk carries over-flow tubes which deliver the H_2O from the top of 1 cell to the bottom of the next below, the H_2O leaving the app. near the top of the lowest cell. The over-flow tubes should be closed at each end and have holes blown in the side at each end for the H_2O to flow through, as otherwise they might be closed by being pushed against a disk. The diam. of the nipple through which the H_2O enters should be smaller than the holes in the overflows in order to avoid danger of two great pressure on the app. J. H. MOORE

"Samson" automatic temperature regulator. ANON. *Engineering* **112**, 307(1921). —The valve controlling the supply of heat is directly actuated by the expansion of a liquid with a high coeff. of expansion, contained in a cylinder in the fluid or chamber to be heated. As the temp. of the substance heated approaches the desired temp. the valve is slowly closed, minimizing after-heating effects. By means of an adjustable piston the vol. of the chamber of the heated element may be varied to give varying cut-off temps. If the temp. continues to rise after cut off, the piston rises against the resistance of a spring, avoiding the possibility of bursting the app. by excess pressure of the expanding liquid. DONALD W. MACARDLE

A thermostat for regulation of heating systems. *Elec. Rev.* (Chicago) **79**, 527(1921). —The thermostat is of the positive type, moving through its entire range instantly and causing a similar motion in the valve or damper from fully open to fully closed. The temp.-sensitive element is a double diaphragm contg. a volatile liquid and constructed in two sections joined in the center and hermetically sealed. The front wall transmits its motion to a lever arm which operates a switching mechanism opening or closing an elec. circuit. Details and illustration are given. C. G. F.

A new electric muffle oven for temperatures up to 1350°. H. SEIBERT. Berlin. *Chem.-Ztg.* **45**, 772(1921); 3 cuts.—A brief description, without dimensions, of an oven made by H. Seibert & Co., Berlin, in which the resistor is nearly pure C so placed that the rectangular horizontal muffle is heated from 4 sides. It may be constructed for use with any kind of current, is easily repared, and an oxidizing or reducing atm. may be held in the app. J. H. MOORE

Benzine extraction apparatus. GG. ILLERT. *Chem. App.* **8**, 145-6(1921).—A brief description of the Ruf extractor, with 1 cut showing the arrangement of the app., which consists of an extractor with charging hopper above it, an oil or fat collector, a benzine container with a safety cooler, and a return cooler for condensing the benzine. J. H. MOORE

New process of centrifugal filtration. W. J. GEE. *J. Soc. Chem. Ind.* **39**, 255-6T (1920).—In commercial centrifuging of liquors, it is not possible to remove more than 98% to 99% of the total solids unless the rate of feeding is so far reduced as to make economical operation impossible. G. utilizes an "exit flow under centrifugal head," evolving an app. which combines centrifuging with filtering by means of a non-choking filter. The filter drum is secured to a base attached to the bottom of a suspended vertical shaft. Rotation is accomplished by a pulley, the ball bearing race being supported by a conical stand. The upper end of the drum is closed by a top plate providing, in operation, a water-tight joint, but having a central opening for charging and held centrally on the spindle by a distributing plate. The container, which consists of 6 vertical rods with blades, extends the whole length of the drum, and is fastened to the top, middle and bottom plates. The drum is thus divided into compartments and the liquid caused to rotate with the drum. Each compartment holds a thin plate, curved to fit the drum and forming a removable lining upon which the solids are deposited. When the centrifuge has been charged and whizzed, the container is slid up, the plates removed and a new set put in the container. The app. is then ready for continuing the operation. A perforated filter cone is fitted to the base and projects into the separator drum. It is covered with a filter cloth held in place by clamps. Advantages claimed for this machine are: const. filtering rate, very clean sepn., etc. P. D. V. MANNING

Pumps for corrosive liquids. ANON. *Engineering* **110**, 253-4(1920).—The severe conditions imposed by most chem. industries make the use of reciprocal pumps out of the question, while the extreme simplicity of the centrifugal pump makes this type desirable. Fe-Si cannot be used for HCl or in processes where contamination of the solns. by Fe is to be avoided. Pb cannot be used for some acids, and solns. containing metallic salts. Ebonite cannot be used for hot solns. and is a bad material to use for the rubbing surfaces of the glands. The best all around material is some siliceous ceramic material of which *Ceratherm* is recommended. This material has a good heat cond. and can be plunged red hot into cold water without cracking. A modified form developed in England has a high tensile strength and is easily manufd. The material forming the body of the pump is cemented to an iron casing and so put together that it is only subjected by the bolts to crushing strain. The stuffing box is usually packed with paraffin soaked wool. The thrust bearing is at the end of the shaft, away from contact with acids. These pumps show high efficiencies. P. D. V. MANNING

Determination of absolute viscosity by the Gümbel viscosimeter (SCHILLER) 2.

Filter. R. WÜSTER. U. S. 1,386,340, Aug. 2. The liquid to be filtered is placed in a container having its bottom formed of filtering material and placed within another container for receiving the filtered liquid.

Electrically heated still. C. G. ADSIT. U. S. 1,386,484, Aug. 2. The still comprizes a vertical retort with a vapor dome at its upper end and having a surrounding heating coil heated by induction from a. c. The app. is adapted for the distn. of *petroleum*.

Apparatus for fractional distillation of liquids. H. F. PERKINS. U. S. 1,386,200, Aug. 2.

Apparatus for evsporating or concentrating wsste waters from molasses or similar liquids. H. G. SCHWARZ. U. S. 1,385,499, July 26. The app. may be heated by waste exhaust gases.

Apparatus for generating terpene ozonide vapor. E. D. KLOTS. U. S. 1,386,410, Aug. 2.

2—GENERAL AND PHYSICAL CHEMISTRY

W. E. HENDERSON AND EOWARD MACK

Chemistry and civilization. CHARLES BASKERVILLE. *J. Ind. Eng. Chem.* **13**, 881-2(1921). **Energy: Its sources and future possibilities.** ARTHUR D. LITTLE. *Ibid* 882. **Human and superior direction of power.** LEO H. BAEKELAND. *Ibid* 882-3. **Theories.** WILLIS R. WHITNEY. *Ibid* 883-4. **Chemistry and life.** WILLIAM J. POPE. *Ibid* 884. **Research applied to the world's work.** C. E. K. MEES. *Ibid* 884-5. **The problem of diffusion and its bearing on civilization.** ERNST COHEN. *Ibid* 885. **Catalysis: The new economic factor.** WILDER D. BANCROFT. *Ibid* 885. —Excerpts from addresses on the occasion of the International Meeting held Sept. 8 during the meeting of British, Canadian and American chemists in New York City. E. J. C.

Chemistry and the state. FRANCIS P. GARVIN. *J. Ind. Eng. Chem.* **13**, 866-73 (1921).—A stirring address before a joint meeting of British, Canadian and American chemists. Sound and comprehensive scientific research and a practical development of the application of the results and discoveries of such research, so important to national welfare, is impossible in any country without an appreciative understanding by the peoples of that country that science in this century is the soul of the prosperity of nations and the living source of all progress. It is the chemist's responsibility to help bring about public understanding of this importance of science to his nation. E. J. C.

Some aspects and problems of post-war science, pure and applied. T. EDWARD THORPE. *Chem. News* **123**, 133-41, 145-6(1921); *Science* **54**, 231-9, 257-66(1921). E. H.

The organization of research in a democracy. R. A. MILLIKAN. *J. Western Soc. Eng.* **26**, 305-14(1921). E. H.

[Joseph Priestley.] C. A. BROWNE. *J. Ind. Eng. Chem.* **13**, 879-81(1921).—A brief address on the occasion of the presentation of a portrait of Priestley (reproduced here), which is to be hung in the Natl. Museum at Washington. E. J. C.

"Caput mortuum" again. EDMUND O. VON LIPPMANN. *Chem. Ztg.* **45**, 801 (1921).—"Caput mortuum" is shown to have been used originally in alchemistic writings as a generic term for any "residue," and not specifically for "red oxide of iron." "*Colcothar*" is derived from the late Greek, and meant a complex decompn. product of vitriol, either green or red. W. C. EBAUGH

Pressure and volume expansion coefficients of helium, hydrogen, and nitrogen. F. HENNING AND W. HEUSE. Phys. Tech. Reich. *Z. Physik* **5**, 285-314(1921).—A careful redetn. of these quantities gives the following. α = vol. expansion coeff., β = pressure expansion coeff. and p_0 = ice point pressure. For He, $10^7\alpha = 36604 - 19p_0$, $10^7\beta = 36604 - 4p_0$. For H, $10^7\alpha = 36604 + 12p_0$, $10^7\beta = 36604 + 17p_0$. For

N, $10^7\alpha = 36604 + 127p_0$, $10^7\beta = 36604 + 134p_0$. Thus the new value for the expansion coeff. of an ideal gas ($p_0 = 0$) is 36604×10^{-7}. F. C. HOYT

Variations in the density of air. A. JAQUEROD AND CH. BOREL. *J. chim. phys.* **19**, 11–28(1921).—See *C. A.* **15**, 2370. E. H.

A rapid method for determining the density of air. GREGORY P. BAXTER. *J. Am. Chem. Soc.* **43**, 1317–8(1921).—The wt. in vacuum of a sealed globe of known exterior vol. is found by weighing the globe under known conditions of temp., pressure and humidity, from which the d. of the atm. at the time of weighing and the buoyant effect of the air upon the globe and wts. are computed. The difference between the buoyant effect on the globe and on the wts. added to the wt. of the globe in air gives the wt. of the globe in vacuum. If the globe is now weighed in air under any conditions the atm. d. may be found by dividing the wt. of air displaced by the globe in excess of that displaced by the wts. (found by subtraction from the wt. in vacuum) by the vol. of the globe less the vol. of the wts. An accuracy of about 0.1% is attainable with a 100-cc. globe. The effect of temp. on the globe is neglected since it is only 0.003% per degree. G. W. STRATTON

Note regarding the melting points of high-melting metals and compounds. ANON. *Z. Metallkunde* **12**, 66–7(1920).—M. ps. as obtained by numerous investigators have been recalcd. to a uniform scale and the results are shown in 2 tables, one of the metals, the other of the high melting silicate and oxide compds. like the clays, porcelain, etc. R. S. W.

Effect of temperature on the form of the surface layer of crystalline selenium. W. GRIPENBERG. *Physik. Z.* **22**, 281(1921).—When Se is cooled between glass plates the surface is not perfectly smooth, although it appears so. There are many small pits (0.1–0.001 mm. in diam.); depth not detd. These appear to be due to crystals whose major axes are perpendicular to the glass plate. The coeff. of expansion is greater on this axis. An electrode, therefore, does not make perfect contact with a Se plate, which may be a reason for the impossibility of making precision measurements. M. K.

Purification of mercury. C. HARRIES. *Z. angew. Chem.* **34**, Aufsatzteil, 359 (1921); 2 cuts.—H. finds the Meyer column unsatisfactory for the removal of base metals, and resorts to oxidation with atm. O at 150–200°, and subsequent distn. *in vacuo*. A stream of air is drawn through the Hg in a round-bottomed flask heated on a sandbath, and the scum of basic oxides is filtered off. The last traces of oxide are removed by shaking with concd. HCl. A well cooled worm condenser between the aeration flask and pump, obviates loss of Hg due to evapn. at this temp. To avoid possible back pressure, H. recommends forcing compressed air through, which simultaneously serves to stir the Hg vigorously. Final distn. is carried out in the ordinary manner, except that the cork stopper of the fractionating flask is made vacuum-tight with a mixt. of glue and chalk. THEO. F. BUEHRER

Purification of mercury. P. H. PRAUSNITZ. *Z. angew. Chem.* **34**, Aufsatzteil, 443(1921).—The method of Harries (preceding abst.) was tried on a 1% Pb-amalgam. On aeration at 150°, a dense foamy mixt. of Hg and PbO forms, from which the Hg is obtained by shaking repeatedly with 25% HNO_3 soln. This mass can also be easily purified by passing as fine spray through a Meyer column. P. does not regard Harries' method an improvement over the Meyer column. He finds the latter, contg. 25% HNO_3, very efficient, though it has the disadvantage of forming hard crusts of $HgNO_3$ which are sometimes difficult to remove. T. F. BUEHRER

The volumes of mercury meniscuses. J. PALACIOS. *Anales soc. espan. fis. quim.* **17**, 275–95(1919).—A cylindrical steel ring was mounted on a carriage capable of being moved in a horizontal direction by means of a micrometer screw. Directly above the ring, on an independent support, was fastened a spherometer provided with a slender

steel point. The ring was filled with very pure mercury and beginning at one edge of the ring a series of measurements of the height of the mercury surface at known intervals were made across the meridianal section of the meniscus. A microscope was used to det. when the steel point of the spherometer was in optical contact with its image on the mercury surface. Readings were made to a precision of 0.0005 mm. Since it is known that the surface tension of a newly formed mercury surface in contact with air changes slowly for some time, series of measurements were made on the same meniscus when newly formed and again several hours later. The change in shape was not measurable. Series of measurements were made with six different rings of different diameters from 1.0 cm. to 2.0 cm. and with several meniscuses of different heights in each. By calculus methods the equation of the meridianal curve was derived and the vol. of each meniscus detd. The following table was then calcd. The values found are in every case slightly greater than those found by Scheel and Heuse by a different method (*C. A.* **4**, 3029). (Also see following abstract.)

Volumes of the meniscuses in cu. mm.

Heighth of meniscus in mm.	Radius of tube in mm.						
	5	6	7	8	9	10	11
0.1	4.0	6.5	9.5	13.1	17.2	21.9	27.2
0.2	8.2	13.2	19.3	26.4	34 6	44.0	54.6
0.3	12.5	19.9	29.0	39.8	52.2	66.3	88.2
0.4	17.0	26.8	39.0	53.3	70.0	88.8	110.0
0.5	21.5	33.9	49.1	67.0	87.9	111.0	138.0
0.6	26.2	41.0	59.3	80.9	106.0	134.0	167.0
0.7	31.0	48.3	69.6	94.9	124.0	157.0	195.0
0.8	35.9	55.8	80.1	109.0	143 0	181.0	224.0
0.9	41.0	63.3	90.8	123.0	161.0	204.0	253.0
1.0	46.2	71.0	101.0	138.0	180.0	228.0	282.0
1.1	51.5	78.8	112.0	152.0	199.0	251.0	312.0
1.2	56.9	86.7	123.0	167.0	218.0	276.0	342.0
1.3	62.5	94.8	135.0	182.0	237.0	300.0	372.0
1.4	68.2	103.0	146.0	197.0	257.0	324.0	402.0
1.5	74.0	111.0	157.0	212.0	276.0	349.0	433.0
1.6	79.9	120.0	169.0	228.0	296.0	373.0	463.0
1.7	85.9	128.0	181.0	243.0	316.0	399.0	494.0
1.8	90.1	137.0	193.0	259.0	336.0	424.0	526.0
1.9	——	——	205.0	275.0	356.0	449.0	557.0
2.0	——	——	217.0	291.0	377.0	474.0	589.0
2.1	——	——	——	307.0	397.0	500.0	621.0

L. E. Gilson

The form of the meridianal section of a mercury meniscus. J. Palacios. *Anales soc. espan. fis. quim.* **18**, 62–5(1920).—The mathematical calcn. of the shape of the mercury meniscus by Verschaffelt (*C. A.* 13, 1173) was checked by substituting in the equations the values found by actual measurements by Palacios (preceding abstract) and found to be correct.

L. E. Gilson

Molecular forces and their electrical interpretation. P. Debye. *Physik. Z.* **22**, 302–8(1921).—Arguments are given in favor of the hypothesis that the attractive forces between mols. are of purely elec. origin. Between the mols. of all substances a mutual attraction exists, due to the polarization which each mol. undergoes in the elec. fields of the others. Depending upon the degree of coincidence of the centers of gravity of their positive and negative charges, mols. are divided into two groups, dipolar

and quadripolar. After considering the behavior of such mols. in elec. fields, D. shows how observations based on the van der Waals equation of state indicate the existence of polarization forces. From an analysis of the H atom the conclusion is drawn that the rotating electron acts as if it possessed a potential energy with respect to the mol. equal to its mean kinetic energy of oscillation. The fact that this energy is necessarily positive explains why there is a universal repulsion between mols. and electrons. Calcn. from the magnitude of this repulsive force gives a value of 0.50×10^{-8} cm. for the radius of the *H atom*. It is perhaps possible to understand on the basis of these polarization forces how *crystal structures* can be stable. E. N. Buntino

Active racemates. Marcel Delépine. *Compt. rend.* **172**, 1049–52(1921).—A crystal composed of *d*-rotary mols. of 1 compd. and *l*-rotary mols. of a compd. isomorphous with it will usually be an active racemate. Among other examples it is indicated that mixts. of the Ca *d*-chloro- and *l*-bromo- and of the *l*-chloro- and *d*-bromocamphorsulfonates ($Ca(C_{10}H_{14}OX.SO_3)_2.6H_2O$; where X = Cl, $[\alpha]_D = \pm 93°$; where X = Br, $[\alpha]_D = \pm 63.8°$) furnish crystals resembling the ordinary chloro and bromo racemates but which have a rotation of $[\alpha]_D = \pm 20°$. It is concluded "that one can call racemic a cryst. structure composed of an equal number of dextro- and levo-rotary mols. The optical activity is only an accessory phenomenon depending upon the nature of the 2 kinds of mols.; it is zero in case these two are simply enantiomorphic." Ralph W. G. Wyckoff

The numerical value of the gas constant. F. Henning. *Z. Physik* **6**, 69–72 (1921).—From a discussion of existing data H. gives as the best value $R = (8.313 \pm 0.003) \times 10^7$ ergs per degree per mol. F. C. Hoyt

Structure in disperse systems. G. Weissenberger. *Kolloid-Z.* **29**, 113–24 (1921).—Dispersoids, more particularly emulsoids, whose concn. exceeds a certain limit tend to form uniform secondary aggregates of the primary particles of disperse phase, probably as a result of a spacial hindering of the free movements of the particles. The primary particles, which are ultramicroscopic aggregates of mols., are very stable and reproducible. Emulsoids exhibit discontinuous, microscopic structures, which are not arbitrary, but of a definite and reproducible character. These secondary structures are built up in a uniform way from the primary particles. In turn, secondary structures may unite to form aggregates of still higher orders. The largest conglomerates may be macroscopic. These structures of higher order are easily broken down, for example by mechanical agitation, shaking, or forcing the soln. through capillaries. If the viscosity of such an emulsion is observed in an Ostwald viscosimeter, it is found to fall off with successive passages through the capillary until a const. value is obtained, the magnitude of which depends upon the size of the capillary. This is believed to be due to the breaking up of the structures of higher order into structures of a size not exceeding the diam. of the capillary. If the dispersoid is then allowed to rest, the viscosity slowly increases again as the structures of higher order are reformed. Expts. on the viscosity of suspensions of the fuller's earth from Gaura, Siebenbürgen (*C. A.* **15**, 184) gave results in conformity with these ideas. F. L. Browne

Sulfide sols. II. Preparation of sols with gaseous hydrogen sulfide. Friedrich-Vincenz v. Hahn. Leipzig. *Kolloid-Z.* **29**, 139–45(1921); cf. *C. A.* **15**, 202.—Ag_2S hydrosols were prepd. by bubbling H_2S through 0.002 *N* $AgNO_3$ soln. The stability of the sols was measured by means of the "violet value," that is, the concn. of electrolyte in millimols per l. which is just sufficient to produce a certain shade of violet after 5 min. standing (about 44 according to Ostwald's color scale). The stability of the sol increased with (1) longer treatment of the soln. with H_2S, (2) more rapid passage of the H_2S through the soln., and (3) higher temp. F. L. Browne

Chemical reactions in mixtures of sols. H. Freundlich and Alexander Nathansohn. *Kolloid-Z.* **29**, 16–19(1921).—When sols having similar charges were mixed,

a series of changes resulted which are probably due to a chem. reaction between the "complexes" in the mixt. The changes of color—brown, wine, red, violet, steel blue, greenish blue, greenish brown, pale yellowish brown—in the reaction between Ag sols and S sols resemble those of photochloride of silver and certainly depend on the presence of "complexes" in the mixt. These "complexes" contain Ag besides S or sulfide. A mixt. of a soln. of H_2S and Ag sol gave similar color changes. Mixts. of S sols and Se sols or As_2S_3 sols and Ag sols gave characteristic changes of color. H. M. M.

Studies on protective colloids. Tenth series: saponin as a protective colloid. I. General colloido-chemical investigation of guaiac-saponin and quillaia-saponin. II. On colloidal gold. A. Gutbier, J. Huber and R. Haug. *Kolloid-Z.* **29**, 19–25, 25–7(1921); cf. *C. A.* **15**, 2223.—(I) The physical and colloido-chemical relations of the two kinds of saponin were essentially the same. Dialysis did not remove the inorg. constituents always contained in the solns. A 1% soln. slowly diffused through the parchment paper. After 3 days standing a ppt. formed in a 1% soln., but in a 0.25% soln. only a slight ppt. formed after several weeks. The viscosity of solns. increased a small amt. with standing and with increasing concn., but was const. for solns. of 0.25% or less. An increase in temp. decreased the viscosity, but when the soln. was boiled for 24 hrs., the viscosity at first decreased and then in 2 hrs. reached a const. max. value. Equal vols. of solns. of HCl or NaCl up to 1 normal did not change the viscosity, but solns. of NaOH increased the viscosity. (II) Saponin solns. proved to be efficient as a protective colloid for gold. Five parts of gold chloride soln. 1:1000 mixed with 20 parts of 1% saponin soln. and reduced with hydrazine hydrate at room temp. gave a reddish violet soln. which even without purification was very stable. When cautiously evapd., it formed a dark red mass, a completely reversible solid colloid, containing 2.2% Au. When 75 parts of the gold chloride soln. was mixed with 50 parts of 0.5% saponin soln. and reduced as before, the resulting stable colloid was dark blue by transmitted and rust-brown by reflected light. The solid contained 30.77% gold. Other concns. gave solid colloids which contained, respectively, 11.87% and 15.21% gold. Colloids of still higher gold content can be prepared but these solids are not completely reversible. H. M. McLaughlin

The coagulation of colloidal arsenious sulfide. The influence of the dilution of the electrolyte and of the concentration of the electrolyte. A. Boutaric and M. Vuillaume. *Compt. rend.* **173**, 229–32(1921).—The velocity of coagulation of arsenious sulfide hydrosol with solns. of KCl, $BaCl_2$, and $AlCl_3$ was measured by the method previously described by the authors (*C. A.* **15**, 2758). Twenty-five cc. of a sol made from a soln. of 5 g. As_2O_3 per l. was dild. to volume v and $(100-v)$ cc. of electrolyte soln. added. (1) When the total quantity of electrolyte in $(100-v)$ cc. remained const., the velocity of coagulation at first decreased as $(100-v)$ increased, finally remaining const. beyond a certain dilu. of the electrolyte. Velocities of coagulation with different electrolytes are comparable only when the electrolyte solns. are sufficiently dil. to attain this constancy of the velocity of coagulation in each case. (2) When the total quantity of electrolyte in $(100-v)$ cc. was proportional to this vol., the velocity of coagulation increased with the quantity of electrolyte soln. F. L. B.

Investigation of the conditions for stability of platinum organosols. Johs. Lindeman and The. Svedberg. *Kolloid-Z.* **29**, 1–16(1921).—A soln. of $HAuCl_4$ was added to Pt organosol and reduced with H_2O_2 (cf. *C. A.* **4**, 1568). Au was deposited on the Pt nuclei, whether abs. alc. or a mixt. of alc. and ether was used as the dispersion medium. The radius of the Pt nuclei, r, was detd. from the relation $r^3 : R^3 = s_g p : s_p g$. The radius of the Pt nuclei after the Au had been deposited, R, was found from the velocity of sedimentation and by the use of Stokes' law. The terms g and p, and s_g and s_p, are resp. the masses and sp. wt. of the Au and Pt. The stability is detd. by considering

the values of r and the coagulation temp. The sols were never entirely stable and changed continuously toward complete coagulation. Temp., Pt concn. and ether concn. influence the velocity of this change, increasing if either factor increases. There is no const. max. temp. limit for the existence of these sols. Since the temp. of coagulation depends rather on the rate of rise of temp., it is better to speak of the critical curve of the sol than of the critical temp. H. M. McLAUGHLIN

Absorption of moisture by gelatin in a saturated atmosphere. CHARLES A. SHULL AND S. P. SHULL. *Am. J. Botan.* **7**, 318–26(1920); *Botan. Abstracts* **7**, 305.—The authors summarize briefly the work of VON SCHRÖDER on the absorption of water by gelatin from liquid water and from a satd. atm. On repeating a part of his expts. they obtained very different results, finding that gelatin absorbed much more water from a satd. atm. than von Schröder reported. Instead of reaching an equil. at a gain of 40% in about a week, this absorption continued steadily until the end of the expt. (47 days), when water equal to over 170% of the gelatin had been absorbed.—Equations for the curves of moisture intake are given. The authors call attention to the difficulty of maintaining a satd. atm., and suggest that the difference between their results and von Schröder's is due to their greater success in this respect. H. G.

Some applications of capillary and electrocapillary chemistry. W. LEWIS. Univ. Liverpool. *Caoutchouc & gutta-percha* **18**, 10773–80(1921).—An explanation of the principles of colloid chemistry, including adsorption, the deductions of Gibbs, the Brownian movements, the theory of Helmholtz, and the principal applications of colloids to industry, such as the coagulation of *rubber*. The text is non-mathematical, and for the general reader. C. C. DAVIS

Critical temperatures of solution of fats in mixtures of ethyl and amyl alcohols. A. J. J. VANDEVELDE. *Bull. soc. chim. Belg.* **30**, 14–6, 58–62(1921).—Expts. were undertaken to det. whether a mixt. of 94% EtOH with isoamyl alcohol (*C. A.* **8**, 2732), which gave critical soln. temps. similar to those of Crismer's EtOH, could advantageously replace the latter. A mixt. which gave with light petroleum the same crit. soln. temp. as Crismer's alc. was found to give lower values with glycerides, and a mixt. which gave with beef fat the same crit. soln. temp. as Crismer's alc., gave, especially with cacao butter and light petroleum, higher values than those of Crismer's alc. The distances between the extreme critical soln. temps. of the substances examd. are greater for Crismer's alc. than for the amyl alc. mixts., which gives the former a greater sensitiveness. The divergences observed with the amyl alc. mixts. seem to be due to the relative soly. of the fats in amyl alc. J. S. C. I.

Influence of temperature on the viscosity of normal liquids. EDM. VAN AUBEL. *Compt. rend.* **173**, 384–7(1921).—The formula $\varphi = m + n \log (\theta - t)$, where φ is the fluidity, t is the temp. observed and θ is the crit. temp. of the liquid, and m and n are consts., reproduces satisfactorily the observed data for PhCl, EtOAc and C_6H_6. The fluidity formula is the exact analog of the vol. formula of Avenarius. By differentiation of the above formula one finds that the increase in fluidity for a given elevation of the temp. is inversely proportional to the distance from the crit. temp. E. C. B.

Determination of absolute viscosity by the Gümbel viscosimeter. L. SCHILLER. *Z. tech. Physik* **2**, 50–2(1921); *Science Abstracts* **24A**, 316–7.—Gümbel has recently (*Z. tech. Physik.* **1**, 72–5(1920)) described a new viscosimeter for the detn. of abs. viscosity. The app. consists essentially of a vessel with circular aperture in the center of the base and a concentric circular disk at a small distance from the aperture. The outflow ensues around the circumference of this disk, and then runs radially between this and the base to the exit. The principal loss in pressure by internal friction then takes place in the narrow space between the two plane plates, flow and discharge ensuing through two concentric circular cylindrical mantles. Gümbel, without derivation

or statement submits the following expression for arriving at the viscosity: $Q = H_{max.} \cdot \gamma . \pi h^3 . \log_e(R/r)/6\eta$, where Q is the outflow in m.^{3} per sec., r the inner radius of the inserted disk, R the external radius, h the aperture width in m., H the liquid height in m., γ the wt. per unit vol. (in kg./m.^{3}), and η the viscosity coeff. in kg. sec./m.^{2}. S. now shows that by accepting Gümbel's assumptions an expression for the viscosity is obtained which deviates in two respects from that given by Gümbel, namely: $\eta = [(H - 0.8854^2) \times 10^{-6} \{Q/(h-h')\}^2] [\{(h \times h')^3 \times 0.5328^3\}/Q]$. S. states that for the detn. of abs. viscosity it is necessary to develop further the theory of the app., and to expt. with liquids of greatly differing viscosities. A comparison is made between Engler's viscosimeter and Gümbel's, greatly in favor of the former, whose theory is stated to be much more rigidly established. H. G.

Use of the Duboscq type of colorimeter for the demonstration of differences in surface tension. FREDERICK S. HAMMETT. Wistar Inst. Anatomy, Phila. *Science* **54**, 172–3(1921).—A new use for the colorimeter of practical value in lab. instruction in the basic phenomenon of surface tension. When H_2O, alc., Et_2O, acetone or toluene is put in the colorimeter cup or beaker and the height to which is it possible to raise the plunger from contact with the surface of the liquid before breaking contact is measured the differences observed are rough indices of the differences in the surface tension of the liquids used. The effect of soap, amyl alc. or picric acid on the surface tension of H_2O also is demonstrated. F. S. HAMMETT

Synthesis of higher order compounds. PAUL PFEIFFER. *Z. angew. Chem.* **34**, Aufsatzteil, 350–4(1921).—A lecture in which synthesis of mol. compds. is advocated (1) for purposes of structural detn. in cases where ordinary substitution reactions cause destruction of the mol.; (2) as sources of information concerning adsorption and crystal structure. Elucidation of the structure of such compds. by the principles of (1) isomorphism and (2) substitution is discussed. (1) is illustrated by the compds. $K_2[Pt(OH)_6]$, $K_2[Sn(OH)_6]$ and $K_2[Pb(OH)_6]$; $K_2[SnCl_4(OH_2)_2]$ and $K_2[FeCl_5(OH_2)]$; $[Mn(OH_2)_4]Cl_2$ and $K_2[BeF_4]$. Under (2) P.'s work upon neutral salt compds. of amino acids and polypeptides and upon quinhydrones is discussed. A. R. MIDDLETON

Reaction velocity in hydrogenations by platinum black. G. VAVON. *Compt. rend.* **173**, 360–2(1921).—Hydrogenation by Pt black in an atm. of H may be followed by noting the vol. of gas absorbed in unit time, which is designated the "global velocity" of the reaction at any moment. The reaction consists of 3 processes. (1) H is dissolved by the reaction mixt. and reaches the catalyst; (2) the reacting substance C diffuses, reaches the catalyst, and reacts with the H; (3) the new compd. $C + H_2$ leaves the surface of the catalyst and diffuses into the solvent. When 2 reacting substances, C and C' are present, the global velocity may remain const. throughout, or, after being const. during the hydrogenation of C, it may diminish or rise suddenly when C' begins to react, depending on whether C' hydrogenates slowly or rapidly compared with C. The absorption of H by the following pairs of compds. was studied in the light of the above considerations: cinnamic acid-carvomenthene, cinamic acid-α-pinene; maleic acid-carvomenthene, maleic acid-α-pinene, and fumaric acid-α-pinene. An increase of velocity was noted with cinnamic acid-α-pinene in AcOEt or Et_2O, but not with EtOH or AcOH, indicating that the solvent also plays an important role. M. R. SCHMIDT

The relation between the occlusive power of palladium for hydrogen and its activity for catalytic hydrogenation. EDWARD B. MAXTED. *J. Chem. Soc.* **119**, 1280–4 (1921); cf. *C. A.* **14**, 10; **15**, 197, 1646.—The author has previously shown that the occlusive power of Pd for H_2 in the presence of occluded H_2S varies linearly with the content of the inhibitant, and also that the activity of Pt for catalytic hydrogenation is a linear function of the content of catalyst poisons. This study was designed to show that, for a given catalyst and inhibitant, occlusive power and catalytic activity stand

in a linear relation to each other. The influence of Pb (as the acetate) on the occlusion of H_2 by Pd and on the catalytic activity of Pd for the hydrogenation of oleic acid were studied by the methods previously described. The occlusive power of Pd for H_2 was found to be a linear function of the Pb content of the Pd. The catalytic activity was also a linear function of the Pb content, down to a certain point of inflexion, at which point most of the catalytic activity had been destroyed. However, "the slope of the linear graphs connecting, resp., the occlusive power and the catalytic activity with the content of inhibitant is not the same. It requires a ratio of 0.17 g.-atom Pb to 1 g.-atom Pd to reduce the occlusive power to one-half its original value, while in order to reduce the catalytic activity to one-half, only about 0.02 g.-atom Pb to each g.-atom Pd is necessary. It appears not improbable that the reason for this lies in the fact that while occlusion of H_2 is not confined to the surface only of the Pd, catalysis is mainly a surface phenomenon. This view is strengthened by the observation that the slope of the poisoning line for catalytic activity varies with the fineness of division of the catalyst,....while the poisoning coeff. for inhibition of the occlusive power does not vary." F. L. Browne

Studies of oxidation catalyzers. I. L. Karczag. *Biochem. Z.* 117, 69–86 (1921).—K. studied the decolorizing effect of 2 drops of H_2O_2 on 2-cc. lots of 0.005% solns. of some 34 org. pigments of known chem. compn. in the presence of 1 drop of $FeSO_4$, $Fe_2(SO_4)_3$, $CuSO_4$, $FeNH_4(SO_4)_2$, $NiSO_4$, $MnSO_4$, $Co(NO_3)_2$, $FeCl_3$, $PtCl_4$ or "ferroamino sulfate." The general summary of the results indicates that the Fe oxidizers oxidize in the cold all the dyes without exception, and with no regard to their chem. constitution or reaction. The structural influence of the dye is a factor in the time taken for decolorization. The Cu oxidizer acts more slowly in the cold and is not significantly affected by the reaction of the medium. Co as a catalyzer is sensitive to acids and works only in neutral soln. It is a stronger catalyzer in the cold than Cu but weaker than Fe'''. Mn is similarly affected by the soln. reaction. Pt and Ni are indifferent towards an acid reaction and are selective oxidizers in that they decolorize some dyes and not others. Three groups of oxidizers are recognizable. In the first group are those compds. which decolorize the dyes in the cold with good O_2 evolution, such as Fe in neutral reaction; these are called the "cold-oxidizers." The second group is composed of those which act best when heat is applied. These include Cu and Mn in neutral soln. and are called the "heat-oxidizers." In the third group there are Ni and Pt, which are elective in their decolorizing activity. In the system pigment + oxidizers + H_2O_2 the cold and heat-oxidizers possess oxidase + catalase types of activities, while the elective group possesses only oxidase powers. They are then designated as oxidizers of the first and second order, resp. II. *Ibid* 119, 16–22(1921).—A study of the catalytic activity of hivalent Fe with the time of decolorization of various dyes in the presence of several ferrous salts and H_2O_2 as an indicator of the stimulation to oxidation It was found that, as with tervalent Fe, the oxidatiou of the dyes by bivalent Fe has no relation to the chem. constitution or the physico-chem. properties of the compds. used, and that the phenomenon occurs spontaneously in the cold, regardless of the reaction of the medium. The significant difference between the catalytic activity of the Fe'' and Fe''' ions is that with the former the decolorization of the dyes is much more rapid. When the Fe'' salt is added to the dye soln. before the addition of the H_2O_2 the reaction is almost instantaneous. When the order is reversed the decolorization is prolonged. This time difference in effect is attributed to a difference in the initial complex formation and reaction between the various components of the mixt. The instantaneous reaction is considered as due not to a sensitization but rather to a spectral ferrous ion action. Other studies on the successive decolorization of mixts. of dyes by $FeCl_3$ and $PtCl_4$ show that there apparently exists a selective action of these

catalyzers in the oxidation of dyes in the presence of H_2O_2. Bivalent Fe is classified as an oxidizing catalyst of the first order. F. S. HAMMETT

Simultaneous reactions of the same probability. F. E. C. SCHEFFER. Univ. Technique, Delft. *Rec. trav. chim.* **40**, 477–87(1921).—In the reaction (1) $R.A.B + C.D \rightarrow R.A.C + B.D$ the group R remains bound to A before and after the reaction and although there is no change in the manner in which it is combined the velocity of reaction depends to a large extent on the nature of R. If one takes a given group R in the reaction (2) $R\vdots CH + NO_2OH \rightarrow R\vdots CNO_2 + H_2O$ he may make changes in the constitution in the vicinity of A which will have the greatest possible influence on the velocity of reaction or by making changes in another part of the mol. this effect may be eliminated. If it is assumed that the groups R and R' satisfy this condition then reaction (1) and (3) $R'.A.B + C.D \rightarrow R'.A.C + B.D$ will have the same velocity and the results of such reactions taking place simultaneously or independently may be discussed with the aid of considerations of probability. But it is not necessary that (1) and (3) be independent. In the mol. $S(A.B)_2$ the $A.B$ groups are equiv. and may react successively, thus (4) $S(A.B)_2 + C.D \rightarrow (C.A)S(A.B) + B.D$; (5) $(C.A)S(A.B) + C.D \rightarrow S(A.C)_2 + B.D$ and the 2 reactions are examples of types (1) and (3). If the $A.B$ groups are sufficiently far apart the transformation of the one $A.B$ group will be independent of the other and the 2 equations may be written thus (7) $S(A.B)_2 \xrightarrow{2K} (C.A)S(A.B) \xrightarrow{K} S(A.C)_2$. The successive reactions of $S(A.B)_3$ with $C.D$ under the same conditions are worked out on the basis of probability and it was found that "the nos. of mols. of reaction products are related as the terms of a binomial of the 3rd degree." The no. of mols. of products of reaction (7) will be related as the terms of a binomial of the 2nd degree. In general "when the reaction takes place in n degrees and for each degree the transformation affects identical atoms or groups of atoms, under identical conditions, the concn. of the original substance and the concns. of the products successively formed are related as the terms of a binomial of the nth degree." Considering the sapon. of fats as an example of $S(A.B)_3$, S. found that the results obtained experimentally by Traub (*C. A.* **12**, 2155) in the sapon. of trilaurin with H_2SO_4 conform approx. with the requirements of probability as discussed in this paper. The case $S(A.B)_3$ is also discussed on the assumption that the 2 $A.B$ groups are not equiv. and the probability of replacement of B by C is not the same. Finally the case $S(A:B_2)_3$ is considered in which the 2 groups bound to S are equiv. but in which secondary reactions are possible because A is bound to 2 nonequiv. B atoms of which one or the other is replaced by C but not both. The nitration of dipbenyl carbonate, which is discussed in the following abstract, is an example of this case. E. J. WITZEMANN

The nitration of phenylcarbonates. J. M. A. HOEFLAKE. Univ. Technique, Delft. *Rec. trav. chim.* **40**, 488–518(1921).—It was the purpose in beginning the nitration of Ph_2CO_3 (A) (*C. A.* **11**, 42) to det. the ratio in which the *o*- and *p*-$NO_2C_6H_4$-groups are formed. The compn. of the nitration product strictly speaking was not considered. *A priori* the formation of *o,o*-, *p,p*- and *o,p*-$(NO_2C_6H_4O)_2CO$ was to be expected. If it is assumed that the 2 Ph groups in A do not influence each other in nitration, Scheffer (cf. preceding abstract) has shown on the basis of probability that the 3 substances will appear in the product in the order *o,o*-, *o,p*- and *p,p*- in the ratio $x_1^2 : 2x_1x_2 : x_2^2$ where x_1 and x_2 are the amts. of *o*- and *p*-$NO_2C_6H_4OH$, resp., as detd. in the nitration product after sapon. The amts. of these phenols found (*l. c.*) was 10.7% *o*- and 89.3% *p*-$NO_2C_6H_4OH$ and the calcd. compn. of the nitration product would be 79.7% *p,p*-, 19.1% *o,p*- and 1.2% *o,o*-, resp. If these nos. should be confirmed experimentally it would prove that the 2 Ph groups are without influence on each other and the results would be a confirmation of S.s' calcns. (*l. c.*). H. attempted to det. the compn. of the nitration product by the f. p. method but found that the *o,p*- isomer

is transformed thus during fusion: 2 *o,p*- $\rightleftharpoons$ *o*, *o*- + *p,p*-, and that the transformation is facilitated by the alk. walls of the glass vessels or especially by mixing with a trace of Na_2CO_3. Under the same conditions the *o,o*- and *p,p*- isomers are stable so that the nitration product constitutes a pseudoternary-binary system in the presence of the catalyst. H. detd. the ternary fusion diagram by using Jena glass tubes for the f. p. detns. The binary fusion curve was detd. by means of a catalyst and a method for the detn. of the compn. of the nitration product was based on the graphic representation of the two sets of results. The detns. were made in a H_2SO_4 bath provided with mechanical agitation by means of an Anschütz thermometer. The Ph_2CO_3 was obtained (Hentschel, *J. prakt. Chem.* [2] **27**, 41(1883)) by passing $COCl_2$ through a concd. aq. soln. of NaOPh and was purified by trituration in dil. Na_2CO_3 and crystn. from EtOH. $(o\text{-}O_2NC_6H_4)_2CO_3$ was obtained similarly from $o\text{-}O_2NC_6H_4OH$. $(p\text{-}O_2NC_6H_4)_2CO_3$ was best obtained by nitrating Ph_2CO_3. An improved method for obtaining phenylcarbonylchloride, PhOCOCl, is described. Phenyl-*o*-nitrophenyl carbonate (**B**) and its *p*-isomer were obtained from PhOCOCl and *o*- and *p*-Na nitrophenolate, resp., as white crystals, m. p. 36° and 127°, resp. The double *o*-nitrophenyl *p*-nitrophenyl carbonate was obtained as the main-product in the nitration of **B**, as a white substance, m. 130.1°. The results showed that the compn. of the nitration product of Ph_2CO_3 satisfies approx. the formula (*C*): *o,o*-:*o,p*-:*p,p*- = $z_1^2:2z_1z_2:z_2^2$ calcd. by Scheffer and it follows that the 2 Ph groups in Ph_2CO_3 have practically no influence on each other. The latter statement was also confirmed by nitrations of the 2 mononitrophenyl derivs. It was shown that the equil. of the 3 isomers 2 *o,p* $\rightleftharpoons$ *o,o* + *p,p* also satisfies the formula *C* deduced for this case in an analogous fashion. E. J. WITZEMANN

Heterogeneous catalysis and adsorption. H. R. KRUYT AND C. F. VAN DUIN. van't Hoff Lab. *Rec. trav. chim.* **40**, 249–80(1921).—When substances undergoing reaction are fixed by adsorption to an adsorbant there is the possibility of a reaction acceleration. If such an acceleration is really produced the sp. characters of a catalyst would depend on its sp. adsorption powers. K. and Helderman had previously found that the sapon. of EtOAc is delayed by charcoal, and K. and v.D. have repeated this work and confirmed the results. The expts. were then repeated with an aromatic ester which is known to be even more strongly adsorbed. *p*-$MeCO_2C_6H_4SO_3Na$ was used because of its soly. in H_2O and it suffered a similar retardation in velocity of sapon. In these cases one of the reagents (the ester) is strongly concd. in the boundary surface but the OH is very much less concd. in this layer. In the liquid, however, the reverse is true. These 2 effects result in a retardation of the sapon. It was, therefore, desirable to choose a reaction in which the 2 reagents will both be concd. in the boundary surfaces because of their great power of being adsorbed. For this purpose the addition of Br to the double bond of Na *p*-sulfocinnamate was tried. In this case also C inhibits the velocity of the reaction. Attempts were made to det. what the influence of the reaction products is on the adsorption of the reagents, since knowledge concerning so-called retardation (*refoulement*) by adsorption is quite vague. The results are given in many tables. After a study of the addition of Br to Na *p*-sulfocinnamate had shown that an incontestable increase of the concn. of the reacting constituents in the boundary surface can cause a diminution in reaction velocity it was clear that the adsorbed mols. are in a state less favorable to reaction than when free in soln. Adsorption is not merely an increase in concn. This conclusion is in agreement with the theories of Langmuir (*C. A.* **10**, 3007; **11**, 2849) and Harkins, Brown and Davies (*C. A.* **11**, 731, 1588) who have observed not only the increase of concn. in boundary surfaces but also orientation. If the adsorbed mols. are not as free as before, their limited movements would diminish their chances of favorable encounter and reactions would be diminished. Moreover, when the boundary consists of C or C compds. and H_2O, the mols.

will be turned with their polar part toward the H_2O. If the reaction involves a non-polar or less polar part of the mol. this part is thus turned away from the surrounding liquid and the substances which it contains. Thus if 2 reagents are more or less polar their positions as detd. by adsorption may result in turning them away from each other. The introduction of the polar SO_3Na group in order to increase soly. results in placing the $CH:CHCO_2H$ and the CO_2Me groups at a disadvantage in reacting with Br and NaOH, resp., by turning the reacting end of the mols. away from the other reagent. Attempts were made to increase the polar character of the $CH:CHCO_2H$ group by using Na *p*-sulfodibromohydrocinnamate, which is more sol. in H_2O than the unbrominated compd., and allowing KI to react upon it to give *p*-$NaSO_3C_6H_4CH:CHCO_2H$, but the velocity of this reaction was also retarded by C, showing that the polar influence of the $NaSO_3$ group still preponderates. To repeat the expts. with the same compds. unsubstituted with $NaSO_3$ was without avail on account of their limited soly. in H_2O. In order to escape this dilemma $CH_2BrCHBrCO_2H$ (cf. Harkins' ideas), which has a polar group on all 3 C atoms, and KI were used. This org. compd. should lie parallel to the surface of contact with the 3 polar groups directed toward the H_2O. In this case C accelerates the reaction to give acrylic acid in the way that it might be expected to on the basis of the above. Further tests of these considerations are being made, since it is important to know if they are correct. The results in hand prove that heterogeneous catalysis is not due solely to an increase in the active mass in the boundary surface. This increase of concn. may be accompanied by an increase or a diminution of the reaction velocity, depending on whether the reagents adsorbed are advantageously placed in the surface. A considerable amt. of data on the isotherms of adsorption of the compds. here studied is given in this paper. The results do not help much with the main problem but will, it seems, eventually give an explanation of the continuous diminution of the reaction velocity due apparently to the reversing effect of the products.

E. J. Witzemann

The equilibria of permutites. F. W. Hisschemöller. Univ. Technique, Delft. *Rec. trav. chim.* 40, 394–432(1921).—Artificial double hydrated silicates of Al in which the base is easily replaced by other metals are called permutites. When Na permutite (NaPer) is placed in a soln. of an NH_4 salt some of the Na is replaced by an equiv. amt. of NH_4 and in the final state at a given temp. the ratio $Na:NH_4$ in the permutite is a function of the concns. of Na^+ and NH_4^+ in the soln. H. has studied the following equil. in detail. (1) $NaPer + NH_4^+ \rightarrow NH_4Per + Na^+$; (2) $NaPer + Ca^{++} \rightarrow CaPer + Na^+$. Singer (*Dissertation*, Berlin (1910) cf. *C. A.* 5, 1668) described the prepn. of permutite from a no. of formulas and H. used the formula $Na_2O:Al_2O_3:SiO_2 = 6:1:9$, which had a high activity. The product used was obtained by extg. the powdered melt with H_2O in a Soxhlet app. By reducing the SiO_2 ratio to 8 a product was obtained in which the Na was almost 100% replaced by NH_4 in 10% NH_4Cl. A com. product supplied by the Permutit-Aktien Ges. at Berlin also was used. 0.5 or 1 g. NaPer or NH_4Per was placed in 100 cc. 0.2 *N* NaCl or NH_4Cl or mixts. and agitated at room temp. for some time. After it had settled 25 cc. were pipeted off and used for the detn. of NH_4. From the NH_4 originally present in the soln. and in the solid the change in the NH_4 content of the latter was calcd. The results are given in tables and plotted in square diagrams somewhat different from those used by Rothmund and Kornfeld (*C. A.* 13, 2823) but similar to that used by Ramann and Spengel (*C. A.* 14, 2010). The plotted results for the transition NaPer → NH_4Per and NH_4Per → NaPer show hysteresis (or false equil.) effects comparable to those observed for the adsorption and loss of H_2O by gels by van Bemmelen and observed with certain silicates by Pratalongo (*C. A.* 6, 447). By repeated transformations NaPer ⇌ NH_4Per at room temp. the hysteresis is removed and the true equil. is obtained; the activity of the permutite is

increased by this treatment. NH_4Per does not lose appreciable amts. of NH_3 when exposed to the air. The position of the true line of equil. is displaced by transformations NaPer $\rightleftharpoons$ NH_4Per repeated with heat. In permutite kept dry for a year after prepn. the position of the false and true equilibria was changed; the hysteresis had diminished but had not disappeared. In this old prepn. the hysteresis had almost disappeared after a single complete transformation of NaPer into NH_4Per. In the transformation NaPer $\rightleftharpoons$ NH_4Per the position of the false and true equilibria is independent of the diln. and the size of the particles. This transformation carried out on an industrial permutite showed great similarity both qual. and quant. to the same transformation with aged permutite. The hysteresis with this material is less marked than with freshly prepd. permutite. When left in the soln. 6 mos. the hysteresis had not been entirely removed. The transformation NaPer $\rightleftharpoons$ CaPer was examd. with the industrial permutite and also showed a chem. hysteresis which is not removed by a single total transformation. The final states depend on the diln., but correspond only qual. to the formula of R. and K. (*l. c.*). The existence of a hysteresis in the transformation of permutites raises the question as to whether this is peculiar to this transformation or whether it exists also for other mixed crystals. In spite of the obvious difficulties H. made some effort to study this question. Such a study for the transformation $BaSO_4 + K_2CrO_4 \rightleftharpoons BaCrO_4 + K_2SO_4$ in which the components are isomorphous proved to be impossible because the transformation is incomplete. H. examines critically recent work in order to det. how to deduce from the theory a formula for the equil. of the permutites. H. has shown that the hypothesis of R. and K. (*l. c.*) is untenable because it requires a break in the curve for the series of Na and Tl permutites and in the series of Na and Ca permutites which does not exist. Some suggestions are made for the explanation of the phenomena of hysteresis on the basis of some considerations on the structure of mixed crystals. E. J. W.

Gas thermometer measurements between −193 and −258°. HENNING. Phys. Tech. Reich. *Z. Physik* **5**, 264–79(1921).—H. makes exact comparison between He and H thermometers. At −193° a He thermometer of const. density with ice point pressure of 76 cm. registers 0.04° higher than a similiar H thermometer. In the neighborhood of the condensation point the deviations of N and A thermometers from the thermodynamic scale are two or three times smaller than would follow from the Clausius-Berthelot equation. Under normal pressure the h. p. of H is 2−52.80°. Accurate calibration of a particular platinum wire is given. F. C. HOYT

Quantitative experiments on boiling under reduced and increased pressures. PAUL WERNER. *Z. physik. chem. Unterricht* **34**, 161–4(1921).—The app. consists of a test-tube partly filled with H_2O and closed with a rubber stopper provided with a thermometer and bent glass tube. The H_2O is boiled at first vigorously to expel all the air, and the test-tube is then connected to a tube 1 m. long, which dips into mercury. As the test-tube cools (an extra test-tube is also used in series to serve as a condenser) a partial vacuum forms. The rise of mercury in the tube indicates the extent of reduction of the pressure in the system. One student notes the temp., another dets. the pressure by the mercury gage. The continuation of the boiling is observed under reduced pressures. The test-tube must be cooled by a freezing mixt. to effect large reduction. For increasing pressures, the arrangement is somewhat more complex and the original must be consulted for details. S. MORGULIS

The vapor pressures of mixtures. ALFRED W. PORTER. *Trans. Faraday Society* **16**, 336–45(1921).—The fundamental relation between the vapor pressures of the constituents of a binary liquid mixt. and the compn. of the mixt. is given by Duhem's differential equation $\mu_a(\partial \log \Pi_a)/(\partial\mu_a) = \mu_b(\partial \log \Pi_b)/(\partial\mu_b)$ where μ_a and μ_b are the molar fractions of the components and Π_a and Π_b are the respective vapor pressures. A

new thermodynamic proof of this theorem is given, assuming that the vapor mixt. follows the perfect gas law, that is, that the partial pressures of the components are additive. This equation was integrated by Margules, from whose soln. it can be shown that $\pi_a = \Pi_a\mu\ e^{\beta(1-\mu_a)^2}$, where Π_a is the value of π_a when μ_a becomes unity. Similarly, $\pi_b = \Pi_b(1-\mu_a)e^{\beta\mu_a^2}$. The exptl. results of Sameshima on the vapor pressures of mixts. of acetone and Et_2O (*C. A.* **12**, 2470) agree very well with the figures calcd. from these equations. The value of the const. β for these mixts. is 0.7414, and it increases slightly as the temp. is lowered. A diagram is given showing the different kinds of curve obtained, when relative vapor pressure is plotted against molar concn. in the liquid mixt., from the equation $\pi_a/\Pi_a = \mu_a e^{(1-\mu_a)^2}$ for different values of β from +3 to −3. When $\beta = 0$ the partial-pressure curve is a straight line; for positive values of β it lies wholly above this line, and for negative values wholly below it. For $\beta = 2$ there is a horizontal point of inflection and for higher values there are two points, on either side of a max., for which the vapor pressure is the same. This is of importance in connection with the equil. of partly miscible liquids. For mixts. of MeOH and glycerol $\beta = 1$; for acetone and oleic acid about 0.5; for ether and oleic acid −0.2. In the case of H_2SO_4 acid-Et_2O mixts., an abnormal curve is obtained; for the lower part of the curve $\beta = -6$, but when the proportion of ether in the mixt. becomes large the curve requires a positive value of β. In such cases as this, and only in such cases, it appears necessary to introduce a chem. hypothesis to explain the phenomena. In the second part of the paper it is shown mathematically that the Duhem-Margules equations can be extended to systems of higher order than the binary.

J. C. S.

Studies on standard cells. JUICHI OBATA AND YUICHI ISHIBASHI. *Researches Electrotech. Lab., Japan* No. 88, 14 pp.(Feb. 1921).—Largely a physical study of the Cu and the Cd standard cells. Acidity has no influence on the temp. coeff. of the Cd cell. The e. m. f. is extremely const. and also the acidity (over period of 1 yr.). Cf. *C. A.* **15**, 3021. C. J. WEST

The role of the activity coefficient of the hydrogen ion in the hydrolysis of gelatin (NORTHROP) **11A**. Kieselguhr for the retention of precipitates (GROSSFELD) (BRAUER) (BRUHNS) **7**. The physical chemistry of the crystallization and magmatic differentiation of igneous rocks (VOGT) **8**. Adsorption capacity of commercial charcoal (ROSENBERG) **11A**. What conclusions may be drawn from the occurrence of liquid inclusions in minerals? (NACKEN) **8**. A new case of anisotropy in the melting point (Müller) **10**.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

GERALD L. WENDT

Progress in photochemistry and photography in 1912–1920. E. VALENTA. *Chem. Ztg.* **45**, 709–11, 733–5, 777–8, 801–3, 805–7, 830–1, 854–5(1921). E. J. C.

Is hydrogen composed of a whole number part (A) plus an auxiliary part (B) and a rotating electron (C)? F. H. LORING. *Chem. News* **121**, 315–8; **122**, 8–9(1921).—A speculation as to whether the ordinary H atom contains in addition to the part (*A*) of at. wt. 1.0000, from which all elements are synthesized, an auxiliary part (*B*) of wt. about 0.0077. H on losing (*B*) might polymerize because of very great activation. The suggestion is made that (*A*) might be placed at the head of Group I and (*B*) at the head of Group VII, helping to fill up these groups. F. O. A.

The distribution of radium emanation in various phases. MARIA SZEPAROWICZ. *Sitzb. Akad. Wiss., Wien, Abt. IIa* **129**, 437–54(1920).—The soly. of Ra Em in water

decreases exponentially with increasing temp. A small minimum occurs in the soly. curve at 93.2. This minimum agrees with the theory of G. Jager (*C. A.* **10**, 551). Ra Em is about 4 times as sol. in benzene as in water. No minimum occurs in the soly. curve for benzene but according to the theory a minimum should occur at 86.9°, which is above its boiling point. The soly. in the solid phase depends upon the physical condit on of the pptd. solid. MARIE FARNSWORTH

The decomposition constant of radium emanation. W. BOTHE AND G. LECHNER. *Z. Physik* **5**, 335–40(1921).—This const. is detd. by comparison with a standard soln. of $RaCl_2$ which had previously been directly compared by the γ-ray method with the emanation. The value obtained was $\lambda = 2.106 \times 10^{-6}$ sec.$^{-1}$. F. C. HOYT

Pressure measurements with electron tubes. W. KAUFMANN AND FR. SEROWY. *Z. Physik* **5**, 319–23(1921).—Low pressures in a 3-element tube can be measured by means of the empirical relation between the grid current (I_g), the anode current (I_a), and the distance from anode to cathode, (d), $p = kI_g/I_a d$. K. and S. find the relation of k to the voltage, using data of Mayer (*C. A.* **9**, 554). This is given in the form of curves that are checked by expt. F. C. HOYT

X-ray work at Schenectady. W. D. COOLIDGE. *J. Röntgen Soc.* **17**, 23–9(1921); *Sci. Abstrs.* **24**, 369.—In a popular lecture before the Röntgen Soc. the author deals with the research work carried out at the General Electric Co.'s lab., so far as this applies to the production of Coolidge's X-ray tube. A detailed description is given of the methods used for the production, from wolframite, of ductile *tungsten* for the manuf. of the electrodes. The high temps. needed render the use of crucibles impossible, and elec. methods of heating are used. The methods used to solder the W to the Cu are described. Experimental results of the action of various residual gases on the tube's working are given. Modern types of *Coolidge tubes* are described. F. P. P.

The reduction of radiographic exposures to one twenty-fifth of the normal amount by means of a new type of X-ray plate. Part I. LEONARD LEVY AND D. W. WEST. **Part II.** T. THORNE-BAKER. *J. Röntgen Soc.* **17**, 55–66(1921).—An X-ray plate has been developed along entirely new lines which, while producing negatives equal in quality to those produced by the regular methods without intensifying screens, permits of a reduction in the time of exposure of about 25 or 30 to one, the plate finely grained and of high sensitiveness to rays of extremely short wave length. The emulsion is hardened and a second coating is put on over the first. Ca tungstate in soft gelatin is used for the latter. The Ca tungstate being in actual contact with the sensitive film acts as a greatly improved intensifying screen. After exposure the coating contg. the Ca tungstate is washed off in warm water (110° F.) and the plate then developed as an ordinary plate. The cost is about one third more than the ordinary plate. Points to be observed in the use of these plates are given. The plates are expected to be especially *useful in taking radiograms of metals and in medicine* where short exposures are necessary. F. P. PHELPS

Further points in the manipulation of Impex plates. LEONARD A. LEVY. *J. Röntgen Soc.* **17**, 104–6(1921).—Details of manipulation are given which overcome certain difficulties which have appeared in the use of the plates. Also it is noted that the ratio of the speed of this plate to the ordiuary plate varies with the hardness of the rays used. For an equiv. spark gap of 4 inches between points the speed ratio is only 5:1, at 5 inches the ratio is 9:1, at 6 inches, 16:1, at 7 inches, 22:1, and at 10 inches is about 35:1. F. P. PHELPS

Atomic scattering of sodium and chlorine. R. GLOCKER. *Z. Physik* **5**, 389–92 (1921).—Bragg (*C. A.* **15**, 1453) has exptly. detd. the variation of the at. scattering of Na and Cl in a rock-salt crystal with the angle between incident and scattered X-ray. In comparing these results with theory for the case of several shells of electrons, B.

has neglected the interaction of the electrons on each other. G. calcs. the scattering if this is not neglected, using the method already developed by him (*C. A.* **15**, 2786). The curves thus obtained agree well with B.'s exptl. curves. The arrangement of electrons assumed is: for Na, 2 in the inner shell and 8 in the outer, and for Cl, shells of 2, 8, and 8. B.'s assumption of radial oscillations thus seems unnecessary. F. C. H.

Dependence of the molecular magnetism of paramagnetic substances on the field strength. G. FALCKENBERG. *Z. Physik* **5**, 210–7(1921).—To test whether the magnetic properties of Fe and Mn salts are dependent on the field strength F. develops a method of prepg. isoparamagnetic solns. A small sealed glass tube of $FeCl_3$ soln. is suspended by a thread in a soln. of the salt under investigation. When the solns. are isoparamagnetic the $FeCl_3$ tube is neither attracted or repelled when the whole is placed between the pole pieces of a magnet. Solns. isoparamagnetic at 3000 gausses were found to remain so to within 0.3 to 1% down to 10 gausses in the case of $FeCl_3$, $FeSO_4$, $Mn(NO_3)_2$ and $MnSO_4$. Other observers have reported a considerable change. There is no dependence on frequency up to 94,000 sec^{-1}. F. C. HOYT

Scattering of light in gases. M. BORN AND W. GERLACH. *Z. Physik* **5**, 374–5 (1921).—B. (*C. A.* **14**, 1421) has calcd. the degree of polarization of the scattered light from a Bohr-Dehye mol. of H, O, or N. Comparison of the theoretical value with Gans' (*Verh. deut. physik. Ges.* **20**, 16(1918)) and Strutt's (*C. A.* **12**, 2488) values shows agreement only in the order of magnitude. F. C. HOYT

Spectrophotoelectrical sensitivity of proustite. W. W. COBLENTZ. Bur. Standards, *Sci. Papers* **17**, No. 412, 179–86(1921).—Each of 2 samples of proustite, Ag_3AsS_3, was connected in series with a high resistance (10,000 to 30,000 ohms), a potential of 1.4 to 4 volts and a d'Arsonval galvanometer. The cond. increased with increase in applied voltage. For const. voltage, the cond. increased with time. The progress of the photoelec. reaction with time was similar to that of other substances, *e. g.*, molybdenite, already investigated. To measure the spectrophotoelec. reaction each crystal was exposed to the radiation emerging from the exit slit of a spectrometer, a calibrated 500-watt tungsten lamp or a 600-watt Cooper-Hewitt quartz mercury lamp serving as the source of radiation. The samples were exposed to thermal radiation stimuli extending from 0.3 μ to 2 μ. The greatest activity occurs between 0.5 μ and 0.7 μ, where there is a rapid decrease in spectral absorption, no reaction being observed for wave lengths greater than 0.7 μ. At 22° the reaction consists of a wide max. in the ultraviolet, with a weak ill-defined max. near 0.6 μ. Decreasing temp. (to −167°) increases the intrinsic sensitivity throughout the spectrum, the max. at 0.6 μ shifting to 0.578 μ where, for low temps., the greatest spectrophotoelectric reaction is localized. C. C. K.

The time interval between absorption and emission of light in fluorescence. R. W. WOOD. *Proc. Roy. Soc.* (London) **99A**, 362–71(1921).—A method is given for measuring the time interval between the absorption of light and the outburst of luminosity in phosphorescence about 1/15,000 sec. later. Much of the work was done with mercury vapor enclosed in an evacuated inverted U-shaped tube, its closed ends being bulbs. The Hg in one bulb is heated to about 180°, vapor is given off and condenses in the other bulb. If, now, the light from an Al spark is permitted to pass through the ascending column of vapor some distance above the Hg bulb a phosphorescent flame is emitted. This flame is cone-shaped, its base being concave to and about 2 mm. above the axis of the exciting bundle of rays. These facts show that the velocity of the atoms of ascending Hg vapor is such as to carry the atom a measurable distance between the absorption of light and its emission in phosphorescence. To det. the time between the two phenomena, a special phosphoroscope was designed. A Bakelite disk 45 cm. in diam. was mounted on the shaft of a synchronous motor. This disk carries contact points to operate the spark source, and also a lens to view the illuminated

phosphorescent object. A movable eyepiece or slit may be shifted laterally to exam. the glow after the illuminated Hg tube has been viewed. Or it is possible to mount the phosphorescent substance, such as uranium glass or crystals of $BaPt(CN)_4$, on the rotating disk and keep the viewing eyepiece or slit fixed and note the effect on images of the illuminated substance and the glow. Both methods yield nearly the same results. From the speed of the disk and the measured shift of the eyepiece, the time elapsing between illumination and phosphorescence can be calcd. For Hg vapor it is about 1/15,000 sec. For $BaPt(CN)_4$ it is about 1/400,000 sec., and for uranium glass it is less than this amount. For liquids, the ascending stream of mols. was formed by forcing them under pressure through a fine nozzle. Sunlight was used to excite the glow. With fluorescence the duration of the glow is less than 1/2,300,000 sec. The method of Abraham and Lemoine permits time intervals of the order 1/400,000,000 sec. to be measured. This method depends on the double refraction of CS_2 or $PhNO_2$ in an electrostatic field. With the latter in an expt. with a crystal of $BaPt(CN)_4$ it was found that the time interval was less than 1/10,000,000 sec. C. C. K.

Temperature and pressure dependence of the dielectric constant and index of refraction. RAGNAR LUNDBLAD. *Z. Physik* **5**, 349–62(1921).—L. investigates mathematically the relations of the mol. resonators of liquids and gases in electrostatic and optical fields, taking into account the interaction of electrons in the same atom and in neighboring atoms. A formula is obtained for the temp. and pressure dependence of the above properties, which allows of calcg. the intermol. distances by means of dispersion data. For H this gives 1.021×10^{-8} cm. for the distance between dispersion electrons. F. C. HOYT

Theory of molecular refraction. II. Free and activated valencies. GERVAIS LE BAS. *Chem. News* **123**, 56–8; cf. *C. A.* **15**, 3589.—Evidence is obtained from a a study of mol. refractivities that each free valency produces a change of about 0.5 in C compds. and similar values for S and N org. compds. Evidence is also obtained for the partial activation of C, S and N compds., the degree of activation and, therefore, of refractivity being influenced in a more or less complicated manner by the presence of neighboring groups, etc. These 3 atoms are so different that an explanation must be sought in the valency electrons. The seats of valence seem to be limited to certain regions of the atom, thereby lending support to the Lewis-Langmuir theory of at. structure. F. O. ANDEREGG

Optical rotary dispersion. T. M. LOWRY AND P. C. AUSTIN. Cambridge Univ. *Engineering* **112**, 33(1921).—For simpler org. compds. the single-term Drude dispersion formula is adequate but for metallic tartrates and quartz the dispersion is usually anomalous, requiring the two-term Drude formula, which fits the observed data within a very small exptl. error. It has long been thought this anomaly might be due to the presence of two different substances. This has been now proved for *d*-tartaric acid by prepg. a large number of substituents which show that the apparently homogeneous acid was really composed of two different substances differing as to sign, rotation and dispersive power. F. O. ANDEREGG

Intensity dissymmetry in the Stark effect of the Balmer lines. A. RUBINOWICZ. *Z. Physik* **5**, 331–4(1921).—Stark and Luneland have shown that lines at equal distances from the undeviated position on opposite sides do not have the same intensity. R. shows that this is not inconsistent with Bohr's conceptions, since his results show there are two different kinds of orbits for the electron system in an elec. field. These are those in which the orbit extends in the direction of the elec. field and those in which it extends in the opposite direction. The different frequency of occurrence of these causes the difference in intensity. F. C. HOYT

Interference measurements in the spectra of argon, krypton and xenon. W. F.

MEGGERS. Bur. Standards, *Sci. Papers* 17, No. 414, 193–202(1921).—The spectra of the inert gases, especially of the heavier ones, contain strong lines which represent wave lengths possessing a high degree of homogeneity and reproducibility and these lines are, therefore, suitable for use as standards of wave length. This paper gives the values of 50 wave lengths in the spectrum of A (3948 to 8521 Å.), 18 of Kr (4273 to 7601 Å.), and 12 of X (4500 to 4923 Å.), all of which have been compared with the wave length of the red radiation from Cd (6438.4696 Å), which is the international primary standard. These wave-length comparisons were made by means of etalon interferometers and most of the values are probably correct to one part in several millions. The elegance and precision of the interferometer methods for wave-length comparisons are demonstrated by the close agreement between values obtained by different observers, and also by the const. frequency differences of many of the lines belonging to combination series. There are only a few cases where independent observers differ by 0.004 Å. or more. From the wave-length measurements in A and Kr, frequency differences are obtained which are const. within the probable error of the measurements. This further confirms the exactness of the combination principle of Ritz. If these frequency differences are regarded as true consts., they testify to the accuracy in relative value of the wave lengths involved. W. F. MEGGERS

The conditions for the emission of spark lines in an electric arc. A. DE GRAMONT AND G. A. HEMSALECH. *Compt. rend.* 173, 278–83(1921).—Using arcs in which the cathode is a rod of carbon or graphite and the anode a button of molten Pb, Sn, or other metal on a thin sheet of Cu of considerable area, the authors find that no spark lines are emitted at the C electrode when it is hot from the steady passage of the arc. If a light air current is directed against the arc so that the amt. of the ionized vapor decreases, then spark lines appear. They become more intense if the arc is retarded by a drop of liquid, say distd. water, placed between the electrodes. They become very intense if the arc is chilled by immersion in liquid air. The conclusion is that spark lines are always emitted when the current of the arc is constrained to pass through a region in which the ionization is weak, such as to oppose a strong resistance to the passage of the current. Thus the emission of spark lines is associated with the existence of strong elec. fields. C. C. KIESS

Wave-length measurements in arc spectra photographed in the yellow, red, and infra-red. F. M. WALTERS, JR. Bur. Standards, *Sci. Papers* 17, No. 411, 161–77 (1921).—Observations were made with a grating spectrograph of 640 cm. radius and 299 lines per mm. The photographic plates were sensitized to yellow, red or infra-red light with pinacyanol and dicyanin. The wave lengths of Ag, Al, Au, Bi, Cd, Hg, Pb, Sb, Sn and Zn are given in international units and to 0.01 Å. The longest wave length measured is that at 10395 Å. in the spectrum of Cd. The work is compared with previous results of others and discrepancies are accounted for as arising from impurities, ghosts or overlapping spectra of higher orders. C. C. KIESS

A new spectrum of cesium. L. DUNOYER. *Compt. rend.* 173, 350–2(1921).—A tube of fused quartz, containing pure Cs, has its ends sealed with parallel quartz windows. Around the tube are a dozen turns of coarse Cu wire to carry high-frequency currents. This tube and coil are placed in an elec. furnace with glass walls. As temp. rises an intense pale blue glow is emitted (at 100°); the color changes and is salmon-pink at 250°. At higher temps. the light becomes less intense and loses color. Lowering the temp. brings back the glow in inverse order. A change in the spectrum accompanies the color change. Under strong vapor pressure at high temps., the spectrum has few lines, among which series lines are prominent. At lower pressures series lines fade out and new lines appear. The new lines contain very few coincidences with lines previously measured in flame, arc and tube spectra, but many with spark lines. The

absorption spectrum of this app. consists uniquely of principal series lines. A list of over 600 lines from 2272 Å. to 5889.2 Å. is given. C. C. KIESS

Crystal structure of iron and steel (WESTGREN, LINDH) 9. Molecular forces and their electrical interpretation (DEBYE) 2. Phosphorescence and melting of the sulfides of group II (TIEDE, SCHLEEDE) 8.

4—ELECTROCHEMISTRY

COLIN G. FINK

Electric furnaces: laboratory types. EZER GRIFFITHS. *Beama* 9, 254–9(1921).—A detailed illustrated review. Cf. *C. A.* 15, 3423. C. G. F.

Electric furnaces for non-ferrous alloys. H. W. GILLETT. *Electrician* 87, 295–7 (1921).—See *C. A.* 15, 1857. C. G. F.

Ajax-Wyatt electric furnace. JOHN B. C. KERSHAW. *Engineer* 132, 139–40(1921).—A general discussion, which contains nothing new. C. J. WEST

New type of induction electric furnace. ANON. *Iron Age* 108, 344–6(1921); illus.—A new induction type of elec. furnace developed by the General Electric Co. has a crucible of simple ring form. The primary winding is located above the crucible where it is entirely out of danger in case the metal should leak out of the crucible. Cooling air is brought up through the center of the furnace, along the center leg of the core, and out horizontally over the primary windings. The roof is bridged across an outer and inner steel ring and can be removed easily. Electromagnetic forces affecting the molten bath (secondary) are of two types: an attracting or pinch force and a repelling or centrifugal force. The pinch effect, acting only on current-carrying portions of the bath, tends to squeeze out radially impurities such as oxides, slags, and gases. The repelling force between the primary and secondary, forces the metal of the bath to the bottom of the crucible, causing impurities (slag) to rise to the top. A denser magnetic flux inside than outside the loop gives a slope to the surface of the molten steel and a circulatory motion in planes perpendicular to the direction of the current. The pinch force also gives a gentle motion to the metal in the direction of the current. The furnace is best supplied with single-phase, low-frequency power by a motor-generator running on polyphase, standard-frequency supply. A 2-ton furnace has been operating over a year. The furnace is rated 250 kw., 2200 v., single-phase, 15 cycles. It has 3 charging doors and a tea-pot pouring spout (pouring metal from below slag line). The rammed lining for the secondary channel is "furnite" (basic material) with pitch. In starting the furnace a cast-Fe ring is placed in the bottom of the crucible and a cast-steel ring is placed on the cast-Fe. The cast-Fe, melting first, repairs any breaks which may occur in the cast-steel ring. One ton of metal is poured every 3.5 hrs. with an av. power consumption in the furnace of 750 kw. hrs. LOUIS JORDAN

Melting steel in a non-ferrous electric furnace. ANON. *Iron Age* 108, 472(1921).—A 2000-lb. Baily elec. resistance furnace was fitted with a 9-in. magnesite brick lining inside the ordinary fire brick lining and tested for its applicability to steel melting. There was no difficulty in holding a 0.05% C steel at a good pouring temp. The max. temp. obtained in the hearth was 1850°. The tests indicate that steel of crucible quality can be made and poured in small furnaces of this type with a power consumption of not over 1200 kw. hrs. per ton, which is economical compared with crucible practice. "Furnaces of this type can be advantageously used to replace a large part of the crucible steel making capacity that is still handled in pots." LOUIS JORDAN

Electric vs. crucible furnaces (for brass melting). H. W. GILLETT. *Metal Industry* 19, 240–2(1921).—Adverse judgment on elec. brass furnaces cannot be based on

conditions in a small rolling mill involving intermittent operation. Costs are itemized and compared for a 1-ton elec. brass-melting furnace operated 24 hrs. per day and crucible pit fires operated 3 shifts per day. The elec. furnace shows a saving of over $3000 on 3750 tons of brass in addition to paying first cost (with interest) of the furnace and equipment. Plants melting very small amts. of brass or bronze may do it more cheaply by electricity or by one of various fuels, depending entirely on local conditions. T. H. A. EASTICK. *Ibid* 241–2—The General Electric muffled-arc furnaces for melting brass are criticized as having complicated and weak hearth construction and electrode muffles, and for the apparent impossibility of stirring the metal. High Zn losses are due to manipulation, *viz.*, temp. and time, and not to the type of furnace or fuel. The comparisons of thermal efficiency should be from fuel to melted metal for both elec. and fuel-fired furnaces. Cf. *C. A.* 15, 3061. LOUIS JORDAN

Electric furnace possibilities in the Western iron industry. R. C. GOSROW. *J. Elec. Western Ind.* 47, 265–7(1921).—An analysis of the opportunities open to the elec. furnace in the Western Fe industry, with data on costs, accuracy of control and flexibility which indicate its advantage in this field. C. G. F.

A new electric arc furnace. E. F. RUSS. *Elektrotech. Z.* 42, 34(1921); *Science Abstracts* 24B, 181.—The Russ elec. arc furnace, which is suitable for the melting of Fe, steel, special and non-ferrous alloys, has an upper electrode terminating in a head much larger than the shaft passing through the roof covering nearly the whole area of the furnace bed. This structure prevents creeping up of the elec. arc, and causes the retention of the heat generated in the metal. The life of the roof is increased with a consequent saving in renewals and in maintenance costs. The distance between the electrode head and the surface of the bath is smaller and a more uniform and steady heat is obtained than in other types. The original article contains a sketch of a 150-kg. model for single-phase current. W. H. BOYNTON

Electrodes for arc furnaces. K. DORNHECKER. *Schweiz. Chem. Ztg.* 1921, 373–7, 385–90.—A detailed exposition. Among the topics covered are: Properties of various metal and C electrodes; advantages of the graphite electrodes; electrode losses; electrode holders; the Ratibor metal core electrodes; electrode nipples. The literature references include the recent German patents. C. G. F.

The electrolytically produced calcium-barium-lead alloys comprizing Frary metal. WM. A. COWAN, L. D. SIMPKINS AND G. O. HIERS. *Trans. Am. Electrochem. Soc.* 40, preprint (1921).—A detailed description is given of the properties, prepn. and structure of Frary metal. This is an alloy of Pb with 2% Ba, 1% Ca and slight amts. of other elements. The alloy is prepd. by electrolysis of a fused bath of chlorides of Ba and Ca, with a molten lead cathode and a graphite anode. After about 3 days the proper amt. of Ba and Ca has been absorbed by the Pb. The metallurgy of binary and ternary alloys of Ca, Ba, and Pb is described for the Pb-rich regions. The Pb-Ba fusion curve is presented up to 6% Ba, and shows 2 components, Pb and Pb_3Ba with an eutectic at 4.5% Ba. Micrographs are given showing the structures of several binary lead alloys, and of the ternary Frary metal. The latter consists of Pb_3Ca crystals embedded in a matrix of Pb (or solid soln.), surrounded by a Pb-Pb_3Ba eutectic. Frary metal compares favorably with the Navy standard babbitt as a *bearing metal*, and shows a less rapid decrease in strength with rise in temp. than do other bearing metals. C. H. E.

Electrolytic solution and deposition of copper. T. R. BRIGGS. Cornell Univ. *Trans. Am. Electrochem. Soc.* 40, preprint (1921); *Chem. Met. Eng.* 25, 685(1921).—B. discusses at length the theories advanced by R. Luther, Foerster, *et al.* and indicates where these fall short. The electrolytic behavior of Cu in solns. contg. Cu ions may be accounted for by 2 electrochem. processes: (1) The change from copper metal to cuprous ion or the reverse; (2) the change from cuprous to cupric ion or the reverse.

When Cu dissolves electrolytically at the anode, cuprous ions are formed first. Similarly, at the cathode, Cu can be deposited only by the discharge of cuprous ions. The cuprous ions formed at the anode may be removed either by electrolytic oxidation or by chemical means, depending upon conditions. If the removal of cuprous ions is entirely electrolytic, Cu dissolves as bivalent metal. If removal is entirely chemical, Cu dissolves as univalent metal. If at the cathode cuprous ions are supplied entirely by electrolytic reduction, copper is deposited as bivalent metal. If cuprous ions are supplied entirely by chem. means, Cu is deposited as univalent metal. This theory has been successfully applied to the electrolytic behavior of Cu in cyanide, chloride, and sulfate electrolytes. The theory is a general one and can be adapted to metals other than Cu. C. G. F.

Electrometallurgy of zinc. W. R. INGALLS. *Trans. Am. Electrochem. Soc.* **40**, preprint (1921); *Chem. Met. Eng.* **25**, 689(1921).—A general comparison is given of the electrolytic and electrothermic methods of producing Zn. It is pointed out that the electrolytic process is here to stay, although mainly dependent upon large scale production owing to the high power cost. The total production of electrolytic Zn is 120,000 tons per yr., or about $^1/_{10}$ the world's total prewar production of Zn. The author ests. that the fuel required for distn. and reduction of a ton of Zn in a modern retort plant will, when burned in an efficient modern power plant, generate sufficient energy to deposit a ton of Zn from a sulfate soln., and that the labor required to produce a ton of Zn electrolytically from a given concentrate will be no more than one-third the labor required by the furnace method. In Norway and Sweden much progress has been made in electrothermic methods. At Trollhattan the Pb-Zn ore is treated at high temp. in an elec. resistance furnace. The Pb-Zn vapor is cooled and redistd. in an elec. arc furnace. Ore smelting furnaces of 12000 kg. per 24 hrs. have been installed in Scandinavia. C. H. ELDRIDGE

Deposition of zinc from zinc cyanide solution. C. J. WERLUND. *Trans. Am. Electrochem. Soc.* **40**, preprint (1921); *Chem. Met. Eng.* **25**, 690(1921).—The cyanide bath is to be preferred in plating practice, although a sulfate electrolyte is best for Zn production from ores. For plating the following bath is recommended, values being oz. per gallon: $Zn(CN)_2$ 8, NaCN 7, NaOH 1 or 2, Na_2CO_3 4, NaI 1, corn sirup 1, gum arabic $^1/_8$; temp. of bath 40–50° voltage, 3–5. Very smooth, grayish white deposits were obtained. The electrolyte does not deteriorate on standing and can be used with a high current density even in mechanical plating units where the cleaning is poor. C. H. ELDRIDGE

Factors influencing the electrolysis of organic compounds. R. FREAS. *Trans. Am. Electrochem. Soc.* **40**, preprint (1921).—Further and more careful research into the electrolysis of org. compds. is recommended. The existence of *active hydrogen*, H^-, is postulated as the substance entering into reduction reactions. Electrode potential is the most important factor influencing the electrolysis; next in importance are current density and temp. Many other factors are enumerated. M. KNOBEL

Electrical purification and precipitation of gases and fumes (Cottrell process). HUBERT THEIN. *Z. tech. Physik* **2**, 177–83, 201–9(1921).—The Cottrell process is dealt with historically and then the mathematical formulas underlying the process are discussed at length; it is shown that concentric cylindrical electrodes ppt. most efficiently. The papers by A. F. Neshit, W. H. Howard, *et al.* are reviewed. C. G. F.

Improvements in the construction of the mercury arc rectifiers. W. HOEPP. *Elektrotechn. Z.* **42**, 1032–4(1921).—A detailed illus. review. C. G. F.

A new apparatus for testing insulation of enameled wires (STRAUBEL) 26. Coated metal for torsion-springs (for electrical apparatus) (U. S. pat. 1,386,834) 9.

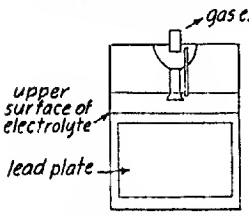
Storage battery. W. E. HOLLAND and J. M. SKINNER. U. S. 1,387,397, Aug. 9. Battery grids are formed of relatively dense homogeneous metal such as Pb.

Storage battery. T. W. THOMSON. U. S. 1,385,507, July 26. Structural features.

Storage battery. R. N. CHAMBERLAIN. U. S. 1,387,350, Aug. 9. The battery is provided with a large safety cap which is readily displaced in the event of explosion of gas within the battery tank.

Storage battery. P. E. NORRIS. U. S. 1,386,946, Aug. 9. Structural features, especially relating to the battery terminals.

Storage battery. C. OLSSON. U. S. 1,386,895, Aug. 9. Structural features.



Storage battery. YEIKICHI MIEDA. Japan 37,032, Aug. 30, 1920. In a portable closed Pb battery a specially designed tube is fitted to the inner lower side of the cover. By this means electrolyte is always maintained under the vent cap in any position without loss or spilling of electrolyte.

Storage battery separators. P. E. NORRIS. U. S. 1,386,650, Aug. 9. Battery separators are formed of woolen fabric supported on a frame of hard rubber, celluloid or other suitable material.

Electrode material for galvanic batteries. T. A. EDISON. U. S. 1,386,095, Aug. 2. Battery electrodes are formed of an agglomerated mass of finely divided Cu oxide held together by a binder of Cu oxide formed *in situ* in the mass, *e. g.*, by the interaction of $CuSO_4$ and NaOH.

Electrolytic diaphragm cell adapted for producing chlorine and alkali from brine. H. H. Dow. U. S. 1,386,094, Aug. 1. Structural features.

Electrolytic cell adapted for electrolysis of salt solutions. G. BAILLIO. U. S. 1,385,655, July 26. Structural features.

Apparatus for electrodeposition of metal. M. M. MERRITT. U. S. 1,387,425, Aug. 9. Articles to be electroplated are placed longitudinally in a flowing stream of electrolyte adjacent to the anodes. The anodes are placed lengthwise of the flow of electrolyte.

Electric furnace adapted for making calcium carbide. W. S. BURCH and W. A. SCHELL. U. S. 1,386,155, Aug. 2. The furnace comprizes 2 sets of electrodes, one at a lower level than the other and supplied with current from independent sources.

Elliptical electric furnace for three-phase current. C. H. VOM BAUR. U. S. 1,385,411, July 26. The furnace is adapted for metallurgical uses.

Refining crude electric-furnace silicon. F. M. BECKET. U. S. 1,386,227, Aug. 2. Crude elec.-furnace Si contg. Fe is crushed and the particles are treated with HF soln. at a sufficiently low temp. (preferably about atm. temp.) to avoid substantial loss of Si while removing most of the Fe.

Oxidizing ferrous metals to effect superficial coloration. T. RONDELLI and Q. SESTINI. U. S. 1,386,076, Aug. 2. The surface of articles formed of ferrous metal, *e. g.*, steel, is subjected to anodic oxidation in a hot concd. electrolyte formed of H_2O and NaOH, with or without nitrates or chlorates or other oxidizing agents.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

Inorganic complex salts. I. Potassium ferric oxalate and potassium cobaltimalonate. WILLIAM THOMAS. Cambridge Univ. *J. Chem. Soc.* **119**, 1140–5(1921).—

Potassium ferrioxalate has the formula $K_3[Fe(C_2O_4)_3].3H_2O$. The corresponding complex salts of Co, Cr, Rh, and Ir have been resolved into optically active components and it was interesting to attempt this for the complex ferri-salt. It was prepd. by dissolving freshly pptd. $Fe(OH)_3$ in a KHC_2O_4 soln. at 35–40°. To prevent decompn. by light, the prepn. and all expts. with the complex salt were carried out in the dark. Attempts to resolve the ferrioxalate by combination with the alkaloid bases were unsuccessful. With the aid of PhNHEt an optically active soln. was obtained but in 15 min. its activity had decreased to one-half its initial value. Potassium cobaltimalonate has not been described. It is prepd. by dissolving $CoCO_3$ in a satd. soln. of KH malonate. The pink soln. was cooled below 0°, excess of PbO_2 added and 50% AcOH poured gradually into the soln. with stirring. The soln. was filtered and dild. with 3 vols. of 97% alc. The ppt. was redissolved and pptd. Its analysis agreed closely with the theoretical values for C, H and Co. The compd. is unstable and attempts to resolve it have so far been unsuccessful. D. MacRae

Catalytic action of hydrogen peroxide on potassium ferro- and ferricyanides. E. A. Lueck. *Apoth. Ztg.* 36, 18–9(1921); *J. Chem. Soc.* 120, 1, 232; cf. *C. A.* **13**, 2823.—Further investigation has shown that the compds. $H_3Fe_2(CN)_{12}$ and $H_4Fe_2(CN)_{12}$ belong to the ferri- and ferro-series, and hence are to be termed octahydroferricyanic and hexahydroferrocyanic acids, resp. The constitution assigned previously to the latter is thus confirmed. The following *salts* of *octahydroferricyanic acid* are described; K, Ca, Cu, Pt, mercuric, uranyl, Ag and Fe. The following *salts* of *hexahydroferrocyanic acid* are described: K, Ca, Cu, Pt, mercuric, uranyl, Ag and Fe. All these salts are anhydrous. W. O. E.

Reduction of inorganic halides. I. Reduction with aluminium. Aluminium triarsenic trichloride. O. Ruff and K. Staib. *Z. anorg. allgem. Chem.* 117, 191–201 (1921).—By heating $AsCl_3$ with Al or P in the presence of $AlCl_3$ at 130–150° for 40 min. there results a brownish red compd., an aluminium triarsenic trichloride of the compn. $AlAs_3Cl_3$. Details of prepn. and analysis are given. The fact that As is easily removed by H_2O, $TiCl_3$, and NH_3, all of which are solvents for $AlCl_3$, leaving finely divided black As, suggests that the As is coördinatively bound in the compd. By heating to 190° out of contact with air a transformation occurs; the compd. turns black, $AlCl_3$ and $AsCl_3$ distil off and a bright gray mixt. of As and arsenide remains behind. $AlAs_3Cl_3$, $\left[Al\langle^{As_3}_{Cl_3}\right]$, is the first example of the coördinative introduction of As into such a complex. It parallels the complex $Al(NH_3)_3Cl_3$. The NH_3 seems to have been replaced by the As. The red color seems to be due to the formation of the compd., since as soon as it is broken up the black elementary As appears. E. H. Darby

The action of cyanides on tetrathionates. A. Kurtenacker and A. Fritsch. *Z. anorg. allgem. Chem.* 117, 202–208(1921).—Gutmann (*Ber.* 39, 509(1906)) and Mackenzie and Marshall (*J. Chem. Soc.* 93, 1726) have both studied the action of KCN on $Na_2S_4O_6$ with disagreeing results. The former finds that Na_2SO_3 is formed slowly only, with an excess of KCN, when heated on the water bath and in the presence of alkali, whereas the latter state that even in dil. soln. the sulfite is formed almost instantly in the absence of alkali and at room temp. The subject is reinvestigated and it is now found that in general the reaction equation of dil solns. is $Na_2S_4O_6 + 3NaCN + H_2O = NaCNS + Na_2SO_4 + Na_2S_2O_3 + 2HCN$. Sulfite formation occurs in neutral 0.1 *N* solns. only if the soln. is boiled for a long time and in alkaline soln. only on heating to boiling, but even then it is not quant. Quant. sulfite formation occurs only if solns. 10–20 times as concd. are heated for an hour on the water bath in the presence of alkali, as was done by G. The observations of M. and M. are, therefore, incorrect. The reaction in dil. soln. may be used for quant. *estn. of* $Na_2S_4O_6$. E. H. Darby

Some unsaturated silicon compounds. H. KAUTZKY. *Z. anorg. allgem. Chem.* **117**, 209–42(1921).—The action of HCl on $CaSi_2$ results in the formation of a mixt. of 3 substances. In order to obtain them pure, the action of alc. HCl, contg. varying amts. of aq. HCl, was studied. Very dil. HCl contg. a large excess of alc. yielded a white, very little sol. cryst. substance of the compn. Si_2H_2O, to which the name *oxydisilin* is given. It has the following properties: Stable to 140°; at higher temps. it is decomposed into gaseous products readily inflammable in air; H_2O decomposes it slowly, more rapidly in heat or light, yielding a self-inflammable gas and H; alkalies and aq. NH_3 cause the reaction to become violent; dry NH_3 reacts above 0° to give nitrogenous compds. which with alc. yield org. Si compds.; it is a vigorous reducing agent—HNO_3 and H_2O_2 react explosively, H_2SO_4 is reduced to H_2S, P_2O_5 to PH_3 in the presence of alc. and many metals are precipitated from solns. of their salts. Treatment of well cooled Si_2H_2O, suspended in CS_2, with a dil. CS_2 soln. of Br gives the yellow compd. *silical bromide*, $(Si_2OH)Br$, so named because it is derived from the new *radical, silical* (Si_2OH). Oxydisilin can be converted into silical derivs. by the action of Cl, $CHCl_3$, CCl_4, C_2H_5I, aq. HCl, H_2SO_3. By hydrolysis of silical bromide, K. prepared dark brick-red *silical hydroxide*, $(Si_2OH)OH$, which is a base forming yellow, readily hydrolyzed *salts* such as halides, sulfate, phosphate, formate and acetate. No solvent for any of the silical compds. was found. These compds. can be oxidized to silicic acid, which is the third product referred to above. The supposed compd. "silicon" obtained by Wöhler (*Ann.* **127**, 264(1863)) and by Hönigschmidt (*C. A.* **4**, 30) as a result of the action of aq. HCl on $CaSi_2$ is undoubtedly a mixt. of the 3 substances isolated by K. Analytical and crystallographic data are given in some detail and it is pointed out that the oxydisilin, the silical compds. and finally the silicic acid are pseudomorphs of the original $CaSi_2$. The structures, $Si_2OH.H$ and $Si_2OH.X$, are proposed for the oxydisilin and the silical compds., resp., but it is suggested that the salts of the latter may be oxonium compds. of the type $Si_2O.HX$. For the unsatd. character of these Si compds. no satisfactory explanation is given; they may be analogous to compds. of bivalent C. E. H. DARBY

Titanium hydride. A. KLAUBER. *Z. anorg. allgem. Chem.* **117**, 243–8(1921).—Previous attempts to prep. TiH_4 by the reduction of TiO_2 in a stream of H have been unsuccessful although an oxyhydride, Ti_3HO_6, appears to have been produced by C. Winkler (*Ber.* **23**, 2, 2662). Cf. C. Renz (*Ber.* **39**, 249(1906)) found that by treatment of TiO_2 with $CHCl_3$ under certain conditions he occasionally obtained a gas which gave titanic acid with H_2O and which appeared to be TiH_4. E. A. Schneider (*Z. anorg. Chem.* **8**, 81) showed that when Ti was heated with a large excess of H a compd. formed which decomposed spontaneously in air. K. attempted to prep. TiH_4 by the electrolysis of a 50% H_2SO_4 soln. using a Ti cathode at 110–240 v. and 0.1–4 amps., but without success. But by working with a discharge electrolysis at 0.2–0.4 amp. and 240 v. with Ti electrodes in the apparatus of Paneth (*C. A.* **15**, 350) suitably modified and 0.1–0.2 *N* H_2SO_4 good yields of TiH_4 were obtained. It is a colorless and odorless gas burning in the air with a colorless flame similar to that of H, with the deposition of TiO_2. The gas may be identified by various reactions by means of which it may also be distinguished from Pb hydride. In the Marsh test Pb hydride gives a gray-brown almost greenish ppt., while TiH_4 gives a gray-black, black metallic, red-brown, violet, or brown ppt. gradually becoming greenish. TiH_4 gives a yellow soln. with H_2O_2, with a crystal of I a reddish orange color which disappears when exposed to NH_3 and a blue soln. with Zn and HCl. E. H. DARBY

Method of recovering mercury from the mercurous sulfate residue of nitrometers. MARCEL LEMIRE. *Bull. soc. ind. Rouen* **49**, 231–3(1921).—The Hg could be regenerated by distn. of the residue with lime in a metallic retort. This was objectionable on

account of the high temp. required. A preferable method was the slow reduction of Hg_2SO_4 by Fe turnings in the cold and a purification of the product by numerous washings with dil. HNO_3. The method described consisted in causing SO_2 to act upon $HgSO_4$ in the presence of H_2O when a black ppt. of "hypo-mercuro-mercuric sulfate" [sulfite?] was formed, $2\ Hg_2SO_4 + 2\ SO_2 + 4\ H_2O \rightarrow Hg_4(SO_3)_2.2H_2O + 2\ H_2SO_4$. On boiling the ppt. decompd.: $Hg_4(SO_3)_2.2H_2O \rightarrow 4Hg + 2H_2SO_4$, yield about 80% of theory. The operation is conducted in a large thick flask, or 2 such flasks in series, furnished with a safety tube and followed by an absorbing flask containing NaOH. About 360 cc. of space should be allowed per kg. of the moist sulfate and 4 to 5 times the wt. of the latter in water should be added. SO_2 is passed 3 to 4 hrs. with occasional thorough agitation. The contents of the flask are then allowed to stand 1 hr., the liquid is decanted off, the residue washed into an evapg. dish and boiled 30 min. After the SO_2 has passed off and the ppt. settled, the liquid is decanted, the finely divided Hg is sprinkled with 400 cc. of H_2SO_4 (66° Bé.) for each kg. of the Hg_2SO_4 treated, and left on the water bath 2 hrs. for the droplets of Hg to assemble in one mass, when the Hg is washed with water and dried with filter paper. L. W. Riggs

Preparation of pure platinum. Howard Wichers. Bur. Standards. *J. Am. Chem. Soc.* **43**, 1268–73(1921).—The method employed consisted in igniting, in the presence of a stream of H, carefully purified $(NH_4)_2PtCl_6$. The samples obtained were tested both spectroscopically and by the thermo-elec. method. The purest samples thus far obtained still show the presence of Ca spectroscopically, but the Ca content is probably not more than 0.0001%. H. Jermain Creighton

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The equilibria of permutites (Hisschemöller) 2. Synthesis of higher order compounds (Pfeiffer) 2.

7—ANALYTICAL CHEMISTRY

William T. Hall

Report of the committee on editing methods of analysis. R. E. Doolittle, *et al. J. Assoc. Official Agr. Chem.* **4**, 540–50(1921).—The changes in the official methods of analyzing fertilizers, soils, inorg. plant constituents, waters, tanning materials, leathers, insecticides, fungicides, foods, feedingstuffs, and drugs that have been made since the 1917 meeting of the Association are given but the original paper must be consulted for details. W. T. H.

Electrometric control in chemical industry. Erik K. Rideal. *Chem. Age* **5**, 232–3(1921).—Possible ways in which electrometric methods of analysis might be utilized in connection with various chem. industries are suggested. W. T. H.

Yellow light in polarimetric determinations. Luis Guglialmelli. *Anal. soc. quim. Argentina* **6**, 497–9(1918).—To obviate the drawbacks of the use of NaCl, Dupont (*Bull. soc. chim.* **17**, 584(1897)) proposed a mixt. of salt and Na_3PO_4; this is found to work very satisfactorily. For its prepn., 1 g.-mol. of Na_2HPO_4 is dissolved in water and treated with 1-g. mol. each of NaOH and NaCl. The soln. is evapd. to dryness and the residue fused. J. C. S.

Kieselguhr for the retention of precipitates. J. Grossfeld. *Z. angew. Chem.* **34**, Aufsatzteil, 411–2(1921).—G. gives reasons for preferring to buy filters already impregnated with kieselguhr rather than prepg. them from common filters as needed. (See Bruhns, *Z. angew. Chem.* **34**, Aufsatzteil, 73). W. T. H.

Kieselguhr for the retention of precipitates. K. Brauer. *Z. angew. Chem.* **34**, Aufsatzteil, 412(1921).—At Charlottenburg kieselguhr as recommended by Bruhns has for a long time been used for the retention of ppts. particularly for filtering samples of turbid urine. W. T. H.

Kieselguhr for the retention of precipitates and turbidities in oil. G. BRUHNS. *Z. angew. Chem.* **34**, Aufsatzteil, 438–9(1921); cf. *C. A.* **15**, 3427.—When fatty acids are set free from soap it is often difficult to get a clear filtrate but the addition of a little kieselguhr serves as a remedy. In fact it was found possible to filter off all of the fat from samples of cow milk and goat milk. An opalescent filtrate was obtained with the former but if AcOH was added this disappeared. B. in reply to criticisms of Grossfeld states that he has been unable to find any reference to the use of kieselguhr for the retention of ppts. in any of the standard textbooks at his disposal. W. T. H.

Color reactions of certain nitro compounds. O. RUDOLPH. *Z. anal. Chem.* **60**, 239–40(1921).—In the examn. of explosives during the recent war, it was noted that the addition of NaOH or NH_4OH to the alc. or acetone solns. caused colorations which were more or less characteristic of the nitro compds. present. The colorations obtained are given in the following table:

Compd.	C_2H_5OH soln. + NaOH.	$(CH_3)_2CO$ soln. + NaOH.	C_2H_5OH soln. + NH_3.	$(CH_3)_2CO$ soln. + NH_3.
o-dinitrobenzene	colorless	(cold) colorless	colorless	colorless
m-dinitrobenzene	colorless	intense reddish violet	colorless	pink to purple
p-dinitrobenzene	colorless	intense yellow	no characteristic color	pale yellow
1,3,5-trinitrobenzene	intense yellowish red	blood-red	yellowish red	blood-red
2,4-dinitrotoluene	deep blue	deep blue	colorless	colorless
2,6-dinitrotoluene	colorless	gradually pinkish	colorless	colorless
2,4,6-trinitrotoluene	deep yellowish red	wine-red to purple-red	light red	light red
1,8-dinitronaphthalene	yellowish red	yellowish red	reddish	reddish

W. T. HALL

From analytical practice. I. Sampling and pipeting of poisonous or caustic liquids. F. MUHLERT. *Z. angew. Chem.* **34**, Aufsatzteil, 442–3(1921).—The liquid from which a sample is to be obtained with a pipet, is placed preferably in a wide-mouthed salt bottle to which a two-holed rubber stopper is fitted. Through one hole a sharply bent piece of glass tubing is inserted which is connected with a rubber pressure bulb. Through the other hole a glass tube is inserted which is a little larger than the bottom tubing of the pipet to be used. A piece of rubber tubing is placed on the pipet tube so that a tight connection is easily made when the pipet is placed inside the second tube of the stopper. By squeezing the rubber bulb, the pipet is filled. If the soln. to be sampled is in a calibrated flask, a stopper with only one hole is used and the glass tubing through which the pipet is introduced is provided with a side arm for connection with the rubber pressure bulb. W. T. HALL

A source of error in the determination of nitrate-nitrogen by the method of Ulsch. F. MACH AND F. SINDLINGER. *Z. anal. Chem.* **60**, 235–8(1921).—Low results in analyses by the Ulsch method were traced to impurities in the Fe powder used. The *ferrum hydrogenio reductum* purchased from a reliable firm was in the form of a very fine powder and contained sulfate, sulfide, carbide and oxide as impurities. It was found that the sulfide content alone sufficed to diminish the usefulness of the Fe for the reduction of nitrates. It is recommended that each new sample of reduced Fe purchased be tested by carrying out an analysis with a nitrate of known purity. W. T. H.

Sensitivity and applicability of qualitative reactions. II. The barium ion. O. LUTZ. *Z. anal. Chem.* **60**, 209–223(1921).—The usual qual. tests for Ba are about

100 times as sensitive as those for K (cf. *C. A.* **14**, 2770). The reactions with Na_2HAsO_4 and with $K_4Fe(CN)_6$ are not sensitive enough to be useful as qual. tests. $(NH_4)_2C_2O_4$ does not ppt. Ba quantitatively except when considerable alc. is added. Na_2HPO_4 in the presence of NH_4OH is a better precipitant and permits the detection of 0.8 mg. Ba at a diln. of 1: 6200. Somewhat more sensitive is H_2SiF_6 or its aniline salt. The much used $(NH_4)_2CO_3$ is only fairly sensitive under the most favorable conditions. $BaCO_3$ tends to form supersatd. solns. and the formation of a ppt. is influenced by the temp. and by the presence of NH_4OH, NH_4 salts, free H_2CO_3 and other substances such as NaCl, Na_2SO_4, $MgSO_4$, $ZnSO_4$ and $Ca(NO_3)_2$. Na_2CO_3 is a better precipitant and it was found possible to detect 0.03 mg. of Ba at a diln. of 1:160,000. Na_2SO_3 proved less satisfactory. Much more sensitive than any of the above reagents was $(NH_4)_2CrO_4$ but the ppt. is appreciably dissolved by solns. of NH_4 salts. H_2SO_4 is the most satisfactory reagent of all. With it a ppt. was obtained when 0.003 mg. of Ba was present at a diln. of 1: 1.6×10^6. The reactions with alkali iodate, the soly. of the chloride and nitrate in concd. acids, alc. or ether, the borax bead and flame tests were not studied but data concerning the sensitiveness of these tests are given.

W. T. Hall

The estimation of sodium hyposulfite. James Hollingsworth Smith. *J. Am. Chem. Soc.* **43**, 1307–8(1921).—By treatment with ammoniacal $AgNO_3$ soln., 2 atoms of metallic Ag are formed by the action of each mol. of $Na_2S_2O_4$ present. The Ag ppt. is filtered off, washed with NH_4NO_3 soln., dissolved in HNO_3 and titrated by the Volhard method. W. T. Hall

Electrometric determination of bromate, dichromate, nitrate and chloride ions. W. S. Hendrixson. *J. Am. Chem. Soc.* **43**, 1309–17(1921).—Accurate results in the titration of bromate were obtained by treating the sample with a known wt. of KI and titrating the excess with $KMnO_4$ electrometrically. In the presence of 2 *N* H_2SO_4 it was also found possible to titrate the bromate directly with KI, although less satisfactorily. Iodide may be titrated directly with dichromate in 2 *N* H_2SO_4 soln. if sufficient time is allowed near the end-point for the reaction to reach completion. Accurate titrations of bromate or dichromate in HCl solns. were not obtained. For the electrometric detn. of nitrite, weighed $KMnO_4$ soln. was run into the titration vessel and the soln. was made approx. 1.5 *N* with H_2SO_4. The stirrer was started and the nitrate added slowly until about 90% of the $KMnO_4$ was decomposed. An excess of iodide was added and the titration finished with $KMnO_4$. The results were excellent. Accurate chlorine detns. were made by treating the original soln. with an excess of Ag, filtering off the AgCl, pptg. the excess of Ag with a known quantity of KI and titrating the excess of I electrometrically with $KMnO_4$. W. T. Hall

The electrometric titration of iodides by means of permanganate. I. M. Kolthoff. Univ. Utrecht. *Rec. trav. chim.* **40**, 532–8(1921).—K. has previously described (*C. A.* **14**, 3204) the use of $K_2Cr_2O_7$, $KBrO_3$ and KIO_3 for the quant. detn. of iodides by the electrometric method. Hendrixson (*C. A.* **15**, 639, 1668) showed that $KMnO_4$ may also be used for this purpose. H. (*l. c.*) and Hostetter and Roberts (*C. A.* **13**, 2319) have used a graphic method for detg. the point of equivalence, but K. found that if the reagent is added drop by drop in the vicinity of the point of equivalence and *E* is detd. each time then this point is detd. simply by the relative variation of the potential. The max. corresponds to the position of the point of equivalence. In this paper K. has used this method. In the results here given other conditions were used than those used by H., and the influence of acidity, diln., etc., was detd. In general K. found that the method gives exact results in the detn. of iodides with $KMnO_4$ in a H_2SO_4 medium. Even with excessively dil. solns. good results are obtained if the H_2SO_4 concn. is at least 0.13 *N*. Although the presence of bromides and chlorides

lowers the fall of potential in the vicinity of the point of equivalence the iodide may still be titrated in the presence of twice as much bromides and 5 times the chlorides equiv. to the iodides present. E. J. WITZEMANN

Test processes for the determination of acids and bases as insoluble salts. G. BRUHNS. *Z. anal. Chem.* 60, 224–29(1921).—Excellent results may be obtained in technical work by making a considerable vol. of soln. to be tested and treating aliquot parts of it with varying vols. of a standard soln. of precipitant until a filtrate is obtained which will give no qual. test for the original substance or for the reagent added. Thus the SO_4^{--} content of sugars has been detd. quickly and accurately as follows: Prepare 200 cc. of sugar soln. contg. 40 g. of sugar and 10 cc. of 12 *N* HCl. Without filtering, pipet off 25-cc. portions into test glasses of about 40 cc. capacity. Prepare a standard soln. of $BaCl_2$ such that 1 cc. = 5 mg. SO_3 and satd. solns. of alum and of $Ba(NO_3)_2$. To the sugar soln. add from a pipet or buret enough of the standard soln. to cause practically complete pptn. Shake well and allow to stand 5 min. Filter, adding a little pptd. $Al(OH)_3$ if necessary to get a clear filtrate, and test with alum and $Ba(NO_3)_2$ solns. to see whether pptn. was complete. With a little skill the correct end-point can be estimated very quickly and a no. of analyses may be carried out simultaneously. W. T. HALL

Indian casein. II. Proportion of fat in casein. Its estimation and elimination. D. M. GANGOLLI AND A. N. MELORUM. Bombay Presidency, Dept. of Industries, *Bull.* No. 4 (1921); *Chem. Trade J.* 69, 244–5(1921).—Alkali is preferable to acid to dissolve casein for analysis because it acts more quickly. To 15 cc. 0.5 *N* NaOH in a separatory funnel add gradually 1.0 g. of 60-mesh casein and shake thoroughly. After complete soln. is effected add Et_2O and det. the fat by evapg. the Et_2O layer to dryness and weighing. If fatty acid is to be included with the fat, acidify the casein soln. and ext. with Et_2O to eliminate fat; ppt. the casein from the sepd. milk, take a sample, dry and analyze; shake the rest of the casein (to remove H_2O) with rectified spirit, filter, shake with abs. EtOH and filter again. Then shake with gasoline in a bottle in a shaking machine, filter, dry and analyze. Fat content in one case was reduced from 0.44 to 0.09%. Casein low in fat has a pale green color; gasoline is recommended for its extn. rather than Et_2O. W. H. BOYNTON

The application of the immersion refractometer to the analysis of aqueous salt solutions. C. A. CLEMENS. *J. Ind. Eng. Chem.* 13, 813–6(1921).—Methods are described by which the % by vol. of dissolved salts can be detd. with the aid of the immersion refractometer. The methods are applicable to solns. of single salts, to mixts. of 2 salts and to mixts. of 3 salts in which the content of one salt is known. W. T. H.

The assay of fluorides; a modification of the method of Thorin and Starck. E. D. GARCÍA. *Anales soc. quim. Argentina* 8, 321–4(1920).—The T. and S. method (*C. A.* 6, 2047) for the estn. of fluorides in aq. soln. is modified, whereby the excess of Ca in the filtrate from the mixed ppts. of CaC_2O_4 and CaF_2 is estd. volumetrically. Knowing the amt. of Ca required for the CaC_2O_4, the amt. of CaF_2 is obtained by difference. Insol. fluorides are first fused with SiO_2 and Na_2CO_3. After treatment of the mass with water, silica is removed by boiling with $(NH_4)_2CO_3$ soln. and the F detd. as above. L. E. GILSON

The analysis of fluorspar. E. D. GARCÍA. *Anales soc. quim. Argentina* 8, 235–41 (1920).—A review of earlier methods is given. In Doyle's method (*C. A.* 13, 2320) an error is caused by the loss of F as AlF_3. In the method proposed, Ca is detd. in the residue from the treatment with AcOH (as in Doyle's method) after removal of silica, Fe, and Al. The amt. of CaF_2 is calcd. on the assumption that all the Ca in the residue is present as CaF_2. Treat 2 g. of the sample with 25 cc. glacial AcOH to dissolve Mg and Ca present as carbonate or silicate. (These may be detd. in the soln. if desired.)

Collect the residue on a filter, wash, ignite at a low heat, and weigh. In a weighed portion of this prepd. residue, det. SiO_2 by volatilization with HF in the usual way. Treat another weighed portion with H_2SO_4 and HF to remove both SiO_2 and F, heating until SO_3 fumes appear. Dissolve the pasty mass in dil. HCl and det. the calcium (and Fe and Al if desired) in the usual way. All the Ca is calcd. to CaF_2 and the amt. in the original sample thus estd. L. E. GILSON

A simplified method for the analysis of commercial hydrofluoric acid. E. D. GARCÍA. *Anales soc. quim. Argentina* **8**, 173–6(1920).—Weigh out a small amt. of the acid, dil. and det. the total acidity of an aliquot part by titrating the *hot* soln., using phenolphthalein indicator. Under these conditions any H_2SiF_6 present reacts according to the equation $H_2SiF_6 + 6NaOH \rightarrow 6NaF + Si(OH)_4 + 2H_2O$. In another aliquot part det. H_2SiF_6 by neutralizing with NH_4OH and boiling gently for some time with an excess of $(NH_4)_2CO_3$ soln. All but a trace of the H_2SiF_6 is decomposed and SiO_2 is pptd. together with compds. of Fe, Cu, etc., if these impurities are present in the acid. Filter off the ppt., wash with weak $(NH_4)_2CO_3$ soln., dry, ignite, and weigh. Det. SiO_2 in the usual way by volatilization with pure HF and calc. the amt. of H_2SiF_6 present in the sample and then the HF by difference. If qual. tests show the presence of appreciable amts. of H_2SO_4, HCl, or other acids these must be detd. and a correction applied to the amt. of HF found. L. E. GILSON

A revison of the optical method for analyzing mixtures of sucrose and raffinose. C. A. BROWNE AND C. A. GAMBLE. *J. Ind. Eng. Chem* **13**, 793–7(1921).—The change in the Herzfeld divisor of the Clerget formula for estg. sucrose from 142.66 to 143 has necessitated a revision of the Creydt formula for analyzing mixts. of sucrose and raffinose. In the course of this revision, the inversion const. of raffinose and the temp. coeff. for the polarization of raffinose before and after inversion have been redetd. The relative accuracy of this revized formula is illustrated in the case of known mixts. of sucrose and raffinose and in the case of known mixts. of these sugars with $K_2C_2O_4$ and asparagine when lead subacetate is used as a clarifying agent. Possibilities of improving the optical method for analyzing mixts. of sucrose and raffinose are also indicated. F. P. PHELPS

The quantitative separation of tin and antimony in the presence of phosphoric acid. MLLE. MOURET AND J. BARLOT. *Bull. soc. chim.* **29**, 743–5(1921).—The proposed method depends upon the pptn. of Sb_2S_3 by H_2S in a soln. contg. considerable H_3PO_4. Dissolve a small quantity of an Sb-Sn alloy in aqua regia, evap. to dryness and take up the residue in a little concd. HCl. Dil. with an equal vol. of water and add 4–4.5 g. of H_3PO_4 for each 0.01 g. of Sn present in a vol. of about 50 cc. Heat, to 80–90° and introduce a stream of H_2S. After 30 min. stop the flow of gas and after 15 min. more, filter and wash with dil. H_2S soln. The ppt. of Sb_2S_3 may be analyzed by any of the standard methods but electrolysis in the presence of $NH_2OH.HCl$ with a current of 0.5 amp. at 2–2.5 volts is recommended. In the filtrate from the Sb_2S_3 ppt., good results may be obtained by pptg. the Sn with cupferron but the ppt. is so bulky that not more than 0.04 g. of dissolved Sn should be present. The cupferron ppt. should be ignited and the residue of SnO_2 weighed. The results of 6 analyses show that the method is suitable for the analysis of solns. contg. 0.1–0.11 g. of Sb and 0.01–0.06 g. of Sn. WILLIAM T. HALL

The determination of tin in cassiterite. HÉRCULES CORTI. *Anal. soc. quim. Argentina* **9**, 44–53(1921).—The proposed method is based upon the well known process of fusing with Na_2CO_3 and S, extg. the Na_2SnS_3 thus formed with water, and pptg. SnS_2 by adding dil. HCl. The SnS_2 is dissolved in concd. HCl and, after boiling off H_2S, NH_4OH is added to ppt. Sn(OH), which is ignited and weighed as SnO_2. L. E. G.

The determination of phosphorus in iron, steel, ores and slags. H. KINDER. *Z. anal. Chem.* **60**, 241–57(1921).—See *C. A.* **15**, 484. W. T. H.

The determination of titanium in iron and steel. THEODOR DIECKMANN. *Z. anal. Chem.* **60**, 230–4(1921).—A colorimetric method, similar in many respects to that of McCabe (*C. A.* **7**, 3580), is capable of yielding accurate values in samples ranging from 0.07 to 22.5% Ti. Dissolve 1 g. of the Fe or steel in dil. HNO_3 and evap. the solns. to fumes after adding dil. H_2SO_4. Boil the residue with dil. H_2SO_4 until all the sulfates are dissolved, filter and wash with dil. H_2SO_4. Add 10 cc. of H_3PO_4, d. 1.3, and a few cc. of H_2O_2. To a similarly prepd. soln. of Ti-free Fe, add standard Ti soln. (3 g. K_2TiF_6 evapd. a few times with H_2SO_4 and diluted with dil. H_2SO_4 to 1 l.) until the color is about the same as in the soln. being analyzed. Dil. both solns. to the mark in a calibrated flask and in Nessler tubes compare the colors in the usual way. The color comparison is most satisfactory when less than 6 mg. of Ti are present in 100 cc. In the samples studied it was found that the SiO_2 ppts. did not contain Ti. With samples rich in Ti it is sometimes desirable to distinguish between metallic Ti and Ti combined with N or C. Metallic Ti is sol. in concd. HCl but the combined Ti is not. With metallic Ti and Fe-Ti it is well to dissolve the sample in HCl in an atm. of CO_2. The Ti^{+++} soln. may then be titrated with Fe^{+++} soln. and the metallic Ti content at once detd. W. T. H.

The determination of nickel and copper on nickel- or copper-plated iron ware. H. KOELSCH. *Z. anal. Chem.* 60, 240–1(1921).—To dissolve off the Ni or Cu coating treat the material with hot $NaNO_2$ soln. contg. a little AcOH. The Fe is made passive by the nitrite and does not dissolve. W. T. H.

The detection of carbon monoxide. C. R. HOOVER. *J. Ind. Eng. Chem.* **13**, 770–2(1921).—A mixt. of pumice, I_2O_5 and $H_2S_2O_7$ reacts with CO and the resulting green color can be used as a measure of the quantity of CO present. Two portable devices are described with the aid of which this reaction can be carried out with fairly accurate results. W. T. H.

Determination of metallic aluminium and of aluminium oxide in commercial metal. JULIAN H. CAPPS. *J. Ind. Eng. Chem.* **13**, 808–12(1921).—The method depends upon the measurement of the vol. of H evolved when the metal in suitable form is treated with either acid or caustic alkali. W. T. H.

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

Determination and study of minerals. A new method for collecting and distinguishing the coats produced by the blowpipe. A. BRALY. *Bull. soc. franc. mineral.* **44**, 8–56(1921) see *C. A.* **14**, 1946. EDW. F. HOLDEN

The determination of the refractive indices of minerals in thin sections by comparison with Canada balsam and collolith. E. LEHMANN. *Centr. Mineral. Geol.* **1921**, 102–12.—L. found in sections contg. an orthoclase that the embedding medium had a lower n than the mineral. Investigation showed that heating "collolith" much above 160° brings about a physical change which also affects the n. The solvents used (xylol, alc., etc.) may be partially retained for years, causing a very substantial lowering of the n. L. recommends use of undiluted material with careful control of temp. O. VON SCHLICHTEN

The colors of minerals and inorganic compounds at low temperatures. M. BAMBERGER AND R. GRENGG. *Centr. Mineral. Geol.* **1921**, 65–74.—Small fragments of minerals and inorg. compds. were suspended in liquid air in a Dewar flask. The liquid air evapd. completely, producing a temp. of −190°. The substance was at once compared with one at room temp. and the color change noted. A large number of sub-

stances were examd. and the results tabulated. Most substances showed color changes, although some showed none. OTTO VON SCHLICHTEN

What conclusions may be drawn from the occurrence of liquid inclusions in minerals? R. NACKEN. *Centr. Mineral. Geol.* **1921**, 12–9, 35–43.—N. shows from phase-rule considerations that the behavior of liquid inclusions on warming gives no information of the temp. and pressure prevailing when the mineral was formed. For CO_2 a certain minimum temp. may be established. For H_2O the fact that the bubble disappears at a temp. below the critical enables one to establish the temp. of formation within narrow limits but pressure remains uncertain. A thorough study of homogeneous and heterogeneous equilibria is necessary before tentative conclusions can be drawn, which in turn demands a physico-chem. investigation of the system involved. O. v. S.

Inclusions in diamond from South Africa. J. R. SUTTON. *Mineralog. Mag.* **19**, 208–10(1921).—The chief foreign minerals upon which the diamond has crystd. include garnet, ilmenite, olivine and pyrite. Zircon and mica are probable inclusions, while cognate inclusions are graphite and bort. Inclusions generally set up fracture or strain in the enclosing diamond. A fracture which reaches the surface without breaking the diamond apart is frequently filled with an intrusion of later crystn. such as calcite, apophyllite, or pectolite. It is suggested that the state of strain may arise in part "from distortion, from instability due to the unconformable foundation of foreign mineral inclusion upon which the diamond is built." W. F. HUNT

Phosphorescence and melting of the sulfides of group II, particularly zinc sulfide. ERICH TIEDE AND ARTHUR SCHLEEDE. *Centr. Mineral. Geol.* **1921**, 154–8.—Pure prepns. of ZnS, CdS, HgS, MgS, CaS, SrS, and BaS were fused in a steel bomb in an atm. of N at 150 atm. pressure, the temp. ranging from 1450–2000°. All except CdS and HgS showed phosphorescence. OTTO VON SCHLICHTEN

Habit and manner of attachment of ice crystals. GEORGE KALB. *Centr. Mineral. Geol.* **1921**, 129–34; cf. *C. A.* **15**, 489.—Temp. controls the habit of ice crystals. Near 0° tabular crystals prevail. Lower temps. favor production of prismatic habit. The plates rest on an edge, the prisms on one end of the principal axis. O. v. S.

The simplest paths of the atoms during gliding in hematite and corundum. A. JOHNSEN. Kiel. *Centr. Mineral. Geol.* **1917**, 433–45.—The paths of the atoms in gliding along (100) and (111) are described. EDW. F. HOLDEN

Artificial twinning in magnetite. ANNI GRÜHN. Kiel. *Neues Jahrb. Mineral. Geol.* **1918**, 99–112.—Pressure produced gliding parallel to (111) in magnetite; the path of the atoms during the gliding is given. EDW. F. HOLDEN

Simple gliding in hausmannite and its optical characters. O. MÜGGE. Göttingen. *Centr. Mineral. Geol.* **1916**, 73–8.—Hausmannite from 5 localities showed twinning lamellas parallel to (101), and crystals from Öhrenstock exhibited gliding phenomena. Sections parallel to (001) show it to be uniaxial, with strong birefringence, and color brownish red. EDW. F. HOLDEN

Artificial gliding in rutile. A. GRÜHN AND A. JOHNSEN. *Centr. Mineral. Geol.* **1917**, 366–74.—Rutile crystals were packed in S powder, and under a pressure of 10,000 to 30,000 atm. gliding along (101) was produced. A comparison of this and the natural gliding in rutile is given. EDW. F. HOLDEN

Diaspore from the Siebengebirge and the island of Naxos. MARIA WATERKAMP. *Centr. Mineral. Geol.* **1916**, 522–5.—Diaspore occurs in transparent yellow crystals at Königswinter in the Siebengebirge in inclusions, in a trachyte, of a corundum schist. They are tabular parallel to (100) and show 3 new forms: α (706), β (796), and γ (201). Diaspore from the island of Naxos, probably an alteration product of corundum, occurs in bright transparent crystals which show the new forms *d* (140), ϕ (350), *g* (27.2.11) and *i* (502). EDW. F. HOLDEN

Intergrown Carlshad twins of sanidine from Laacher See. R. BRAUNS. Bonn. *Neues Jahrb. Mineral. Geol.* 1917, 45–9.—Small transparent sanidine crystals occur in druses in cavities of an altered alkali syenite. Besides parallel groupings of the crystals, there are interpenetrating Carlsbad twins, in which *y* is greatly developed. The feldspar is probably of pneumatolytic origin. EDW. F. HOLDEN

The change caused by isomorphous mixtures in the angle (001)Λ(010) of plagioclase. F. RINNE. Leipzig. *Centr. Mineral. Geol.* 1916, 361–3.—R. shows that the straight line relation between chem. compn. and the value of the angle (001) Λ (010) in the plagioclases does not hold at other than ordinary temps., but is represented by a curved line, as with other angles at room temp. EDW. F. HOLDEN

The change in the crystal angles of related substances, caused by increase in temperature. II. F. RINNE AND R. GROSSMAN. Leipzig. *Centr. Mineral. Geol.* 1917, 73–82; cf. *C. A.* 9, 1020.—On heating to 500° diopside and hornblende show similar changes in the crystal angles and axial ratios. For diopside from the Piedmont; at 20° $a:b:c = 1.09213:1:0.58931$, $\beta=74°10'9''$; at 500° $a:b:c=1.08762:1:0.58604$, $\beta=74°3'57''$: for hornblende from Monte Somma; at 20° $a:b:c=0.54826:1:0.29377$, $\beta=73°58'12''$; at 500° $a:b:c=0.54766:1:0.29333$, $\beta=73°52'38''$. For hypersthene from Pauls Island, $a:b:c$ at 17°=1.02952:1:0.58685, at 500° 1.02593:1:0.58629. Data are also given on the change in prism angle in anthophyllite from Labrador. EDW. F. HOLDEN

Note on the riebeckite of Evisa, Corsica; and on the composition of similar sodic amphiboles from other localities. J. ORCEL. *Bull. soc. franc. mineral.* 43, 232–43 (1920).—An analysis of riebeckite from a pegmatite in riebeckite granite gave: SiO_2 49.70, ZrO_2 trace, TiO_2 0.62, Al_2O_3 2.00, Fe_2O_3 13.14, FeO 21.16, MgO trace, MnO 0.43, CaO 0.20, Na_2O 8.54, K_2O 2.15, H_2O at 110° 0.15, H_2O at 800° 1.90, F 0.17, less 0.07 O=F, sum 100.12%; approx. $8\ SiO_2.3FeO.Fe_2O_3.2Na_2O.H_2O$. Sp. gr. 3.40. EDW. F. HOLDEN

Monticellite crystals from a steel-works mixer slag. A. F. HALLIMOND. *Mineralog. Mag.* 19, 193–5(1921).—The crystals are from ½ to 1 cm. in length and 1 to 2 mm. in thickness. They are prismatic in habit and show the 3 forms (010), (110), and (021); orthorhombic, $a:b:c=0.4382::0.5779$. The crystals are transparent, very pale brown in color, with little or no pleochroism and have parallel extinction. Sp. gr. 3.20. $\alpha=1.663$; $\beta=1.671$; $\gamma=1.680$ (prism method). $2V=74\frac{1}{2}°$. The chem. analysis reveals 16.5 mol. % of olivine present in solid soln., the influence of which is shown in the d. and the mean *n* as well as in the increased values of $a:b$ and $c:b$ and in the larger birefringence. W. F. HUNT

Phenacite from the granite at Hilbersdorf, Reichenhach, Oberlausitz. M. HENGLEIN. *Centr. Mineral. Geol.* 1921, 193–5.—Phenacite composed of the two rhombohedra $(10\bar{1}1)$, $(\bar{1}012)$ is found in druses in the granite, attached to orthoclase, quartz and penninite but beneath or included in chlorite. OTTO VON SCHLICHTEN

Investigations of a zonally colored tourmaline crystal. HERMANN TERTSCH. Vienna. *Centr. Mineral. Geol.* 1917, 273–89.—This paper is a study of the development of the crystal's faces during the growth of a tourmaline crystal as revealed by the form of the differently colored zones. EDW. F. HOLDEN

The cause of the steel-like luster of ilvaite. O. MÜGGE. Göttingen. *Centr. Mineral. Geol.* 1917, 82–4.—Thin films of goethite, resulting from alteration of the ilvaite, give it a steel-like luster. EDW. F. HOLDEN

Water content of heulandite. K. H. SCHEUMANN. *Ber. Verhandl. Sachs. Akad. Wiss. Leipzig* 73, 3–113(1921).—The results of this elaborate study are shown in the figures of 18 analyses, 15 charts of curves, and hundreds of detns. of H_2O in the mineral under different conditions, the figures of which are assembled in more than 15 tables.

Summary: The water-content curves of heulandite [av. compn. $6SiO_2.Al_2O_3.CaO.5.5H_2O$] in the *tx* field are, up to 6 mol., almost continuous lines; they show complete reversibility. The dehydrated equal wts. are also arranged in the same way. The 6-mol. stage is characterized by a stronger indentation of the water-content curves; the optical inhomogeneity of metaheulandite here adjusts itself. This stage appears as of stable type within the metaheulandite series and shows similarity to a true hydrate. By a stronger dehydration below the 6-mol. stage and a temp. of 186 to 246° hysteresis occurs; the rehydration is retarded. The hydration curves of hysteretic metaheulandite show a definite arrest of the mol. proportion stage. The final equal wts. of the hydrations arrange themselves in straight or nearly straight lines. When the lattice reaction of metaheulandite takes place at lower temp. the entrance of hysteresis within certain temps. is prevented. The hydration process is conceived as a crystallotropic lattice reaction and not as an adsorption process, in the sense of the sponge theory. Portions of all the compds. are contained in all the water. The constant total effect of the hydrating process appears as functions of inner-balanced chain like pseudobinary systems whose action is dependent upon deformation of the lattice. The inner deformations are the result of the crystallotropic kind of hydration process and the specific crystal structure function of the H_2O group, which distinguishes zeolites with their proportional part of hydration from the true hydrates. The inner hydration equil. is of the kinetic sort. L. W. Riggs

Anglesite from the Tintic District, Utah. E. H. Kraus and A. B. Peck. *Neues Jahrb. Mineral. Geol.* **1916, II,** 17–30.—Anglesite occurs on quartz crystals in cavities in a siliceous rock which contains galena. Sp. gr. = 6.350. The crystals are of 4 types: (1) prismatic, (2) pyramidal, (3) tabular, and (4) domatic. Two new forms λ (210) and Δ (441) were observed, as well as the doubtful forms R (12.13.156) and (450), which also would be new. Edw. F. Holden

A new occurrence of kieserite crystals. H. Grandinger. Leipzig. *Centr. Mineral. Geol.* **1917,** 49–51.—Four new forms, *w* (011), *m* (010), *z* (112) and *s* (774) were found on clear white crystals of kieserite from Hildesheim. Edw. F. Holden

A supposed twin of copper sulfate. O. Haas. *Bull. soc. franc. mineral.* **43,** 228–32 (1920).—H. shows that supposed twins of $CuSO_4 + 5H_2O$ described by Boeris in 1905 are parallel groupings on (010) with the relation of the face (001) of one individual to the face 100 of the other accidentally close to parallelism in B.'s specimen. E. F. H.

Contributions to the mineralogy of Colombia. Max Bauer. Marburg. *Centr. Mineral. Geol.* **1916,** 481–7.—This paper is a review of a work published in 1915, "Contribucion al Estudio de los Minerales de Colombia" by R. L. Codazzio of the Univ. of Bogota. Descriptions are given of the emerald deposits of Muzo; of large pseudomorphs of chromite after garnet, with pitchblende, tourmaline, mica and orthoclase in a contact zone between pegmatite and gneiss at Arboledas; and of concretions in the sandstone of Bogota, contg. at different localities wavellite of several varieties, vivianite, ludlamite, and dufrenite. Edw. F. Holden

The Troup, Texas meteorite. J. A. Udden. Univ. Texas. *Proc. U. S. Nat. Museum* **59,** 471–6, plates 2(1921).—This meteorite fell on April 26, 1917, about 3 miles north of Troup near a boy who was plowing and who heard the meteor and "saw it smoking" after the fall. The noise of the meteor was reported by several observers from 15 to 47 miles distant. The original stone weighed about 2.25 lbs., measured approx. 15 × 5 × 4.5 cm., and was shaped somewhat like a moccasin slipper. The color of the fresh surface is gray showing rusty dots when exposed to moist air. The texture is fine grained and chondritic, showing small light oval grains on a polished surface. Among these grains are many small particles of Fe and pyrrhotite, the latter being well shown by immersing a polished surface in $CuSO_4$ soln. Chem. analysis by

Schoch and Stullken gave SiO_2 39.68, Al_2O_3 3.59, Fe (metallic) 3.10, FeS 8.00, FeO 22.27, CoO 0.42, MnO 1.24, CaO 2.03, MgO 4.30, Na_2O 3.86, SO_3 8.23, P_2O_5 0.51, C (graphite) 0.80, H_2O at 110° 1.10, ignition loss 0.90, sum 100.03%; sp. gr. about 3.6. The rock is not strictly uniform in compn., the above results representing somewhat of an av. **Mineral composition and structure of the Troup meteorite.** GEORGE P. MERRILL. *Ibid* 477–8(1921).—M. suggests that the amt. of metal (3.1%) given in Schoch's analysis is smaller than one would be led to suppose from the appearance of a polished surface, and that perhaps the material used for analysis did not correctly represent the character of the stone as a whole. Under the microscope the stone presents an extremely variable character with areas of interlocking olivines and enstatites which suddenly give way to other forms. Throughout the entire mass and within the chondrules themselves are areas of maskelynite, with some interstitial areas of colorless $Ca_3(PO_4)_2$ (merrillite). L. W. RIGGS

Silver-lead deposits of the Keno Hill area, Mayo district, Yukon. W. E. COCKFIELD. Can. Dept. Mines, *Summary Report 1920, part A*, 1–6. **Salmon River district, British Columbia.** S. J. SCHOFIELD AND GEORGE HANSON. *Ibid* 6–12. **West coast of Vancouver Island between Barkley and Quatsing Sounds.** V. DOLMAGE. *Ibid* 12–22. **Coquihalla area, B. C.** C. E. CAIRNES. *Ibid* 23–41. **Limonite deposits in Taseko Valley, B. C.** J. D. MACKENZIE. *Ibid* 42–70. **Reconnaisance between Taseko Lake and Fraser River, B. C.** *Ibid* 70–81. **Eutsuc Lake district, B. C.** R. W. BROCK. *Ibid* 81–94. **Lardeau map-area, B. C.** M. F. BANCROFT. *Ibid* 94–102.—The location, accessibility, topography and general geology of the areas mentioned in the 8 papers listed above, are given. At Keno Hill several mines are being worked for galena. In the Salmon River district the ores fall in 3 main groups: low-grade complex type with values for Cu, Pb and Zn, a type rich in Ag, and a type with high Au values. On the west coast of Vancouver Island, Au, Cu, Fe, Mn and marble occur but for some years there has been no mineral production of any kind. Cu will soon be shipped from a mine near Sidney Inlet. The chief mineral deposits of the Coquihalla area in the present decreasing order of importance are Au, Ag, Cu, Mo, and Mn. Ten mines or prospects for Au and 10 for the other minerals mentioned are described. In the Taseko valley deposits of bog iron ore are found in 7 localities. Analyses of 12 samples show Fe to range from 44 to 51.25% and a total estd. tonnage of over 600,000. Metallic minerals have been found in both the Eutsuk Lake district and Lardeau map-area. L. W. RIGGS

Iron ore resources of Europe. MAX ROESLER. U. S. Geol. Survey, *Bull.* 706, 148 pp.(1921).—This paper is the outgrowth of a report compiled for use at the Peace Conference. In order that estimates might be made reasonably uniform the deposits were divided into 3 classes, *viz.*, "Known" ore which is or can be profitably mined now; "Probable" ore which may be mined hereafter as judged from the location and character of the deposits; "Possible" ore includes ores too deep or of too low grade for profitable mining under present methods. Improvements in methods or an advance in price may change the status of these ores. The distribution, production and consumption of Fe are given for each European country. Of the Fe reserves in Europe, France is given 35.2%, United Kingdom 18.2, Sweden 12.5, German Republic 11.1, Spain 5.0, Central Russia 4.2, Norway 3.8 and the remaining 10% is allotted to 15 other countries. In 1913 the production of the leading countries was: German Empire 26.7%, France 20.4, United Kingdom 15.0, Spain 9.1. The "Fe in ore mined per man per year" in 1913 ranged from less than 300 tons in Germany outside of Lorraine Annexée, in England and in Spain, to 395 tons in Sweden. In U. S. the corresponding figure was 590 tons. The annual output per blast furnace was England 28,000 tons, Germany 55,500, U. S. 120,000. Lower costs of wages and transportation in 1913

enabled Europe to compete with America, notwithstanding the more efficient production of the latter country. If the Fe ore resources of Europe are set at 1, the present indications for the other continents are N. America 3, S. America 2, Asia 0.75, and Africa 0.166. Further explorations in Asia and Africa may greatly change these figures.

L. W. RIGGS

The Almadén quicksilver mine. C. DE KALB. *Econ. Geol.* **16**, 301–12(1921).—D. describes briefly the deposits, methods and costs of working them, and the production of this famous old Hg mine. CHAS. W. COOK

The ore of the Almadén mine. F. L. RANSOME. *Econ. Geol.* **16**, 313–21(1921).—A microscopic examn. of specimens of ore from the Almadén mine leads R. to conclude that the cinnabar occurs essentially as a replacement of quartz and sericite and that it has not to any considerable extent been deposited in the interstices of an originally porous rock. The deposit is not to be classed with those in which the cinnabar occurs as an impregnation of a porous sandstone.

Black Lake asbestos area. WYANT D. HUBBARD. *Eng. Mining J.* **112**, 365–8 (1921).—The geologic and petrographic origin of asbestos is described. Mining is generally of the open-pit type. Suggestions for reducing the cost of operations are given. The Black Lake district is potentially rich because of inexhaustible ore and a monopoly of the market, but practically poor because of inefficient handling of labor.

L. W. RIGGS

Phosphate industry. I. Sources of supply of mineral phosphate. W. PACKARD. *J. Soc. Chem. Ind.* **40**, 288–90R(1921).—The nature of the deposits, grade of rock, production and in some cases the probable reserves of phosphate minerals are described for Florida, Tenn., N. Africa, Belgium, France, Christmas Island in the Indian Ocean, and several Pacific Islands. Most of the production figures are for the year 1913. Undeveloped deposits in Morocco, Palestine, and Algeria are briefly described.

L. W. RIGGS

The origin of African phosphates. P. FAERREGA. *L'echo mines metallurgie* **47**, 334–5(1919); *Bull. Agr. Intelligence* **10**, 828–9.—A review in which it is shown that the beds of phosphates are interstratified with limestone. The deposits were formed on a seashore or in a shallow sea; they are of sedimentary or pseudo-sedimentary origin; marine organisms and chem. action of the sea having evidently helped in their formation. The av. Tunisian analysis shows Ca_3PO_4 60–68%, $(Ca, Mg)CO_3$ 12%, Fe_2O_3 and Al_2O_3, 1–2%, SiO_2 6%, CaF_2 up to 6% and H_2O + org. matter 4%. W. H. ROSS

Origin and composition of certain oil shales. REINHARDT THIESSEN. Pitt. Expt. Sta., Bur. Mines. *Econ. Geol.* **16**, 289–300(1921).—A preliminary report on the microscopical study of oil shales, which was undertaken with the hopes of establishing a definite correlation between the results of the microscopic examn. and those of distn. expts. The Chocolate shale of the Devonian of Illinois was made the basis of the study. Oil shales from Indiana, Ohio, Kentucky, Tennessee, New York, Nevada, Utah and Scotland were also examd. The material was examd. in thin sections and the org. matter was freed from the mineral matter by means of a mixt. of HF, HNO_3 and HCl and examd. separately. Conclusions: (1) As far as examd., oil shales do not contain oil as such; (2) oil distd. therefrom has been derived from org. matter contained in them; (3) all identifiable org. matter consists of plant matter or degradation products; (4) the org. matter consists essentially of spores and cuticular matter in varying proportions together with some woody degradation products; (5) no animal matter has been recognized; (6) although the work already done is insufficient to form the basis for positive conclusions, it would seem that oil shales of different geological history, compn., structure and physical characteristics should yield different distn. products and require different methods of treatment. CHAS. W. COOK

Ospwagan Lake—Burntwood River area, Northern Manitoba. F. J. Alcock. Can. Dept. Mines, *Summary Report 1920, part C*, 1–6. **Rat River route from Three Point Lake to Southern Indian Lake, Manitoba.** *Ibid* 6–13. **Terminal moraine of the Seal-Churchill Divide.** *Ibid* 13–9. **Maskwa River Cu-Ni deposit, Southeast Manitoba.** W. S. McCann. *Ibid* 19–30.—In these 4 papers the geography and geology of the regions mentioned are described. So far but few metalliferous deposits have been located in this region, the most promising being the Maskwa River Cu-Ni deposits whereabout 150 claims had been staked up to July 1920. The principal metallic minerals are pyrrhotite, pentlandite and chalcopyrite. L. W. Riggs

Northeastern part of Labrador and New Quebec. A. P. Coleman. Can. Dept. Mines, *Memoir* **124**, 56 pp.(1921).—The geographic and geologic features of the region are described including the flora and fauna. A description of the fine *labradorite* is given and the possibility of quarrying this rock for decorative stones is suggested. Cu ores are reported. The commonest metallic mineral is pyrite which occurs in large deposits, one of which was worked prior to 1906. *Red and yellow ocher fit for paint* was found. Graphite is the most abundant nonmetallic mineral. While no large deposits of economic minerals have yet been found, but little search has so far been made. L. W. Riggs

Mineral resources of the French Alps. E. Roch. *Bull. official direction recherches sci. ind. inventions* **1921**, 294–6.—R.'s notes are based on 2 papers of W. Kilian, "Alpes economiques," March and June 1920. A popular account is given of the mineral possibilities of the French Alps. No figures are stated and no mines or prospects are described. L. W. Riggs

The physical chemistry of the crystallization and magmatic differentiation of igneous rocks. II. J. H. L. Vogt. *J. Geology* **29**, 426–43(1921); cf. *C. A.* **15**, 2813. —This part deals largely with the ternary system $CaMgSi_2O_6$:Ab:An and the sequence of crystn. between the pyroxene minerals and plagioclase. The conclusion is reached that the sequence of crystn. of plagioclase and pyroxene depends upon the relative amts. of the 2 minerals, for the crystn. commences with the solidification of the mineral present in excess of a certain limit. W. F. Hunt

Monazite-bearing granite from the trachyte tuff of Königswinter. K. Busz and M. Waterkamp. *Centr. Mineral. Geol.* **1917**, 169–72.—This granite is composed of feldspar, quartz, biotite, and essential pyrite, with sharp crystals of monazite, which were measured on the goniometer. Edw. F. Holden

An eruption of hornblende andesite in the Malay archipelago. H. A. Brouwer. *Compt. rend.* **173**, 240–2(1921).—The rock, which was elevated above the surface of the ocean by a submarine eruption west of Mahengetang in 1919, is exceptional among recent products of volcanic action in the Malay archipelago, which are pyroxene andesites, or basalts. This rock is a hornblende andesite and free from pyroxene, in which the fresh hornblende forms numerous phenocrysts, not reabsorbed. These with the phenocrysts of plagioclase zones, principally labradorite rich in glassy inclusions of gaseous bubbles, are coated with a glassy mass. The SiO_2 content is 59.4%. The probable reasons for hornblende appearing in place of pyroxene are discussed. L. W. R.

Two lamprophyre dikes near Santaquin and Mt. Nebo, Utah. G. F. Loughlin. U. S. Geol. Survey, *Professional Paper* **120-E**, 1–8(1918).—The rocks are dark gray to black, dense and porphyritic. Microscopically the rocks of the northern dike consist of a glassy ground mass crowded with phenocrysts of augite, biotite, olivine, magnetite, minute crystals of apatite and some feldspar. Chem. analysis gave SiO_2 45.59, Al_2O_3 12.02, Fe_2O_3 3.84, FeO 5.05, MgO 7.09, CaO 10.21, Na_2O 1.82, K_2O 3.90, H_2O+ 3.59, H_2O- 1.64, CO_2 1.91, TiO_2 1.67, P_2O_5 1.33, MnO 0.16, BaO 0.20, SrO 0.16, S 0.13, sum 100.31%; sp. gr. 2.755. The rocks of the southern dike in thin sections

show phenocrysts of biotite, augite, apatite and magnetite in a ground mass of feldspar. Alteration products are pyrite, calcite, chalcedonic quartz, chlorite and hematite. Sp. gr. 2.68. L. W. RIGGS

The French eclogites, their mineralogic and chemical composition, and origin. Y. BRIÈRE. *Bull. soc. franc. mineral.* **43**, 72–222(1920).—This is a detailed account of French eclogites, with some new occurrences noted. They are composed of almandite and the pyroxene, omphacite, with accessories. The omphacite is green, colorless in thin plates, sometimes feebly pleochroic, plane of the optic axes parallel to (010), $Z\wedge c = 36°$, sign +, $2E = 140°$; analysis shows it to be high in Al_2O_3 and Na_2O, hence it may be called a jadeitic augite. Sp. gr. = 3.31. Several analyses of eclogites and associated minerals are given; pyroxenites and amphibolites accompanying the eclogites are described. The eclogites are shown to be metamorphosed basic intrusives; their compn. is similar to that of gabbro and diorite. EDW. F. HOLDEN

An amphibolite with garnet, olivine, and hypersthene. Y. BRIÈRE. *Bull. soc. franc. mineral.* **43**, 300–3(1920).—This rock occurs near Uzerche in Correze, associated with eclogite. An analysis is given. EDW. F. HOLDEN

Episyenite with clinochlore from Souk el Arhaa, R'arh, western Morocco. R. ABRARD. *Bull. soc. franc. mineral.* **43**, 221(1920).—A. describes a rock composed almost entirely of clinochlore and albite. EDW. F. HOLDEN

Some eruptive rocks from R'arh, western Morocco. R. ABRARD. *Bull. soc. franc. mineral.* **44**, 57–9(1921); cf. *C. A.* **14**, 1949.—Near Souk el Arbaa are found: (1) an episyenite, green, and composed of albite and actinolite altering from pyroxene, (2) an ophite of andesine and augite altering to serpentine, (3) an actinolite-albite schist formed by dynamic metamorphism. These differ markedly from the country rocks. EDW. F. HOLDEN

Inclusions of calcareous and siliceous rocks in the basalt of the "Blaue Kuppe bei Eschwege." H. ROSE AND O. MÜGGE. *Centr. Mineral. Geol.* **1921**, 97–102.—The calcareous inclusions show garnet with $n_D = 1.9114$; augite, probably fassaite, a little christobalite, wollastonite, magnetite and apatite. The siliceous inclusions show small crystals of quartz, tridymite, bronzite with glass inclusions, rutile, chalcedony and much pyrite. OTTO VON SCHLICHTEN

Ottrelite and carpholite schists from the Harz. O. MÜGGE. Göttingen. *Neues Jahrb. Mineral. Geol.* **1918**, 75–98.—This paper contains a petrographic description of a sericite-ottrelite schist, a quartz-chlorite-ottrelite schist, a sericite-carpholite schist, and a sericite-carpholite-ottrelite schist; with an analysis of each. These rocks occur in a belt 33 km. in length, west of Griefenhagen. EDW. F. HOLDEN

Reconstitution processes in shales and phyllites. ALFRED BRAMMALL. **Chemical analyses.** H. F. HARWOOD. *Mineralog. Mag.* **19**, 211–24(1921).—A description of certain petrographic methods devized for a detailed study of the above rocks. Microscopic study was assisted by comminuting the rock specimen and examg. the particles after they had been freed from chloritic and carbonaceous matter. Analyses were also made of fractional exts. of the groundmass. The trend of reconstitution in shales, slates and phyllites is towards a metastable ternary system of white mica, chlorite and quartz. The CaO content was of special interest. In some of the slates the mica is rich in CaO, but as the mica recrystd. a large portion of this is lost. It is suggested that the CaO lost to the mica is fixed mainly in the titanite encrusting or replacing the ilmenite. W. F. HUNT

The micro-petrography of the rock-gypsum of Nottinghamshire. W. ALFRED RICHARDSON. *Mineralog. Mag.* **19**, 196–207(1921).—Two theories have been proposed for these deposits, (*a*) segregations of $CaSO_4$ once widely distributed, and (*b*) original saline residues. Recent field work indicates that both modes of origin are represented.

Microscopic examn. reveals a wide range of structure but in general supports the view that the main seam originated by sedimentary deposition, modified by some segregation during deposition, and that the nodular types are concretionary in origin. The metamorphic characters noted are secondary effects of pressure resulting in the hydration of the anhydrite, which forms the core of the nodules of gypsum. W. P. HUNT

New determination of carbon dioxide in water of the Gulf of Mexico. ROGER C. WELLS. U. S. Geol. Survey, *Professional Paper* 120-A, 1–16(1918).—Summary: The detns. of CO_2 in water of the Gulf of Mexico recorded in this paper show that the total CO_2 increases with the depth, that is, with decreasing temp., and the amts. found are very near though slightly below those required for equil. with atm. CO_2 as calcd. by Fox's equation. Detns. of the total concn. of base held in balance with the carbonate and bicarbonate radicals were also made; this quantity apparently increases slightly with decreasing temp. The data presented do not permit an exact evaluation of the "free" CO_2 in the water, but a consideration of the uncertain factors upon which computation of the free CO_2 rests indicates that the amt. is probably so small in the Gulf water that no appreciable error is made by expressing the total CO_2 found as a mixt. of carbonate and bicarbonate. At any rate, the constituents thus detd., taken in the form of salts and dissolved in the appropriate amt. of pure water, would reproduce the Gulf water under the conditions existing when the samples were collected. L. W. RIGGS

The Colorado-Utah petro-shales (BENSON) 22.

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

The position of the metallurgical industries of northern and eastern France: their destruction and reconstruction. L. GUILLET. *Trans. Iron Steel Inst.* (advance proof) 1921, 16 pp. E. H.

Copper in 1919. H. A. C. JENISON. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part 1, 537–614(preprint No. 21, published Sept. 8, 1921). E. H.

Platinum and allied metals in 1920. JAMES M. HILL. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part 1, 37–50(preprint No. 6, published Sept. 9, 1921). E. H.

Effect of costs on South African gold mining. BRUNO SIMMERSBACH. *Chem. Ztg.* 45, 790–2(1921).—Gold recovery of the Rand shows a decline of from 9,296,618 oz. in 1916 to 8,154,172 oz. in 1920. Ores of less than 6.5 dwt. gold per ton cannot be profitably worked. Twenty-five mines, representing over 38,300,000 tons of ore, are below this figure. Cost of recovery during the first half 1915 was 17s. 6d. per ton, last quarter 1919, 23s. 9d., middle of 1920, 25s. 5d. per ton ore. W. A. MUELLER

Agitation in flotation. FREDERICK G. MOSES. *Mining Scientific Press* 123, 477–8(1921).—Agitation in flotation has 3 functions: (1) Mixing of oil or reagents in the pulp, (2) aeration, (3) increasing circulation of the pulp in the flotation app. The first function is improperly called emulsification; any tendency towards emulsifying of oil and water should be avoided, for this reason both salt and acid are often added as they have a tendency to destroy the stabilizing effect of emulsifying reagents. The second function is necessary as the air (1) increases the surface tension or air-water interface so that the froth can float, (2) gives air-water interfaces to which the sulfides may attach themselves, (3) when associated with oil tends to attract the sulfides, (4) gives an upward direction to the pulp, bringing the sulfides in contact with the froth. Air may be added to the pulp by mechanical agitation, positive

pressure, negative pressure or by the production of some insol. gas within the pulp itself. The four methods of incorporating air into flotation pulp form the basis of as many different types of flotation methods, the principles of which are given in detail by M.
A. H. HELLER

Roasting and chloridizing of Bolivian silver-tin ores. M. G. F. SÖHNLEIN. *Trans. Am. Inst. Mining Met. Eng.* No. 1073, 60–4(1921).—Discussion. Cf. *C. A.* **15**, 45.
H. L. OLIN

New blast furnace of the Crane Iron Works at Catasauqua, Pa. RICHARD PETERS, JR. *Blast Furnace and Steel Plant* 9, 577–80(1921); *Iron Age* 108, 814–6(1921).—An illustrated description. E. H.

New 600-ton blast furnace plant. ANON. *Blast Furnace and Steel Plant* 9, 588–97 (1921).—An illustrated description of the plant of the Trumbull-Cliffs Furnace Co. at Warren, O. E. H.

The synthetic preparation of foundry iron and its properties. T. BRONN. *Stahl u. Eisen* 41, 881–8(1921).—By the addition of a P-rich iron high in C, to a basic steel, a synthetic foundry iron can be prepd. which is equal in properties to Swedish charcoal iron. R. S. DEAN

Chemical reactions in the foundry cupola. Y. A. DYER. *Iron Age* 108, 259–62 (1921).—The compn. of air and combustion of coke are discussed from the volumetric and the thermal standpoints, together with the effect of air and CO_2 in the cupola and their control by the height of the fuel bed. The range of flue gas analyses at critical points in melting zone is given. The reactions are (1) oxidation of C to CO_2, (2) reduction of CO_2 by C to CO, (3) decompn. of moisture by C to CO and H_2. The heat balance of the cupola is discussed and the balance sheet of materials per 2000 lbs. charge is given.
W. A. MUELLER

Characteristics of foundry cokes and slags. Y. A. DYER. *Iron Age* 108, 407–9 (1921).—Bee-hive and by-product cokes are compared, with a discussion of ash analyses. Requirements for foundry cokes are given, with tests for sp. gr., shatter test, crushing strength, cell and wall structure. As fluxes the forms of $CaCO_3$, $MgCO_3$ and F are discussed, with analyses. Principles of slagging in cupola are given. Slags are compared, with analyses and their effect on the iron produced, also the theoretical compn. of slag to be approached. W. A. MUELLER

Electric steel foundry. GEO. H. MANLOVE. *Foundry* 49, 426–9(1921).—A straight line foundry in which the Fe enters at one end and travels steadily in the same direction has been developed by the Chicago Steel Foundry Co. Steel is made in a 3.5-ton, 3-phase elec. furnace, which has a removable top permitting dropping the entire charge into the furnace from special buckets. Provision is made for preheating the elec. furnace charge with crude oil. Heats require about 1.5 hrs. with an av. power consumption of 600 kw. hrs. per ton. A special feature of the foundry is the use of a tractor-drawn train of dump cars, which carry sand from the hopper to the molding floor and return to the shake-out grate (beside the sand-conditioner hopper) with a load of sand and castings, thus giving a "loop" service. The sand is handled in a subway extending across the foundry at right angles to the line of travel of the castings. This subway runs from the sand storage to the sand-conditioner elevator; it contains the facing-sand mixer, the hopper from the shake-out grate, magnetic separator, and an elevator to the sand conditioning app. which is at the top of the foundry building. LOUIS JORDAN

The Canadian steel industry and the direct process. NOEL STATHAM. *Iron Steel Canada*, May 1921.—A short survey of present status of steel industry in Canada. Nova Scotia with 35% and Ontario with 65% are the chief iron-producing districts. The Bourcoud open-cycle direct process is discussed. The process involves 3 steps: (1) producing high-temp. reducing gas, (2) reduction of ore by special furnaces, (3)

melting of sponge iron formed. Plans of proposed plants and results and cost figures compared with other processes are given. W. A. MUELLER.

Method of deoxidizing high-nickel steel. C. B. CALLOMON. *Foundry* **49**, 590–1 (1921).—Sound, homogeneous castings contg. 36% Ni, 0.5% C, 0.5% Mn, and 0.25% Si can be made in elec. or basic open-hearth furnace. Steel scrap and grade A shot nickel are charged together. A few shovelfuls of lime are thrown on the charge and, as it melts, more is added to keep the slag basic. Al is not efficient as a deoxidizer for the melted alloy steel. It causes sluggishness of the bath and brittleness of the finished material. Mg is used finally but other deoxidizers precede it. If a spoon test shows much oxide when broken, C is added as coke breeze to an elec. furnace charge or as pig iron to an open-hearth one. After about 20 min. mill scale is added to remove the excess of C. Iron ore is not permissible in the elec. furnace. Its action is too violent and mill scale is more efficient. When the bath is quiet, add Mn or Fe-Mn. Bring to pouring temp. and add Fe-Si. Tap into ladle and complete deoxidation by introducing in stick form, well below the surface of the melted metal, a max. of 3 oz. of metallic Mg per 100 lbs. of steel. JAMES O. HANDY

The manufacture of shells in Canada during the war 1914–1918. H. W. B. SWABEY AND R. GENDERS. *Trans. Iron Steel Inst.* (advance proof) **1921**, 17 pp. E. H.

Crystal structure of iron and steel. ARNE WESTGREN AND AXEL E. LINDH. Univ. Stockholm. *Z. physik. Chem.* **98**, 181–210(1921).—The paper deals with an X-ray spectrographic investigation of the crystal structure of Fe and steel. The results of Hull (*C. A.* **12**, 2004), that the atoms of pure Fe at ordinary temp. (α-Fe) are arranged on a centered cubic lattice, have been confirmed. At 800–830°, *i. e.*, within the so-called β-Fe interval, the atoms are grouped in the same way as in α-Fe. Since allotropy of cryst. solids is synonymous with polymorphism, β-Fe cannot be regarded as a special modification of Fe. In both austenite and pure Fe, which is stable at 1000°, the crystals have a plane centered cubic lattice. This is also characteristic of γ-Fe, and constitutes a fundamental difference between α- and γ-Fe. In martensite the Fe appears in the form of the α modification. This is likewise the case in rapid-drawn steel of ordinary compn. which has been hardened at 1275°. H. JERMAIN CREIGHTON

The transformation in iron at the Curie point. P. DEJEAN. *Compt. rend.* **173**, 412–14(1921).—A rod of very mild steel 120 cm. long by 2 cm. diam. was placed in a long solenoid. A small standardized test coil was placed around the central part of the rod and the change of flow caused by reversing the current in the solenoid was measured. The rod was then replaced by 120 cylinders 1 cm. long and 2 cm. diam. and the current in the small test coil recorded for different strengths of field (250, 500, 750 and 1000 gauss) corresponding to an insulated space between each cylinder of 0.065, 0.27, 1.2, 2.6, and 5.0 mm., resp. From these data a set of 4 curves, one for each strength of field, was prepd. by plotting the intensity of magnetization of the rod as a function of the thickness of insulation between the cylinders. This group of curves shows marked analogy to the set prepd. by Curie by plotting the intensity of magnetization as a function of the temp. The apparent discontinuity in the magnetic properties which is produced at the Curie point is very easily explained as one continuous action, *i. e.*, the progressive transformation of an α-magnetic form into a β-isomorphic form, or simply the progressive dispersion of the elementary magnets by progressive elevation of the temp. The temp. at which the rapid falling off of magnetism occurs corresponds to a certain extent to the removal of the elementary magnets but not to the total disappearance of these magnets. Otherwise the elevation of the temp. of the Curie point with increased strength of field would not be explained. F. W. COBB

The equilibrium diagram of the iron-silicon system. TAKEJIRÔ MURAKAMI. *Science Reports Tôhoku Imp. Univ.* **10**, 79–92(1921).—By means of magnetic and thermal

analyses, as well as microscopic observation, the Fe-Si alloys contg. less than 32.7% of Si are thoroughly investigated, and the equil. diagram obtained by Guertler and Tammann is revized. In this system, 2 compds., Fe_2Si_2 and FeSi, are found. The former is magnetic, with its critical point at 90°, while the latter is non-magnetic. An alloy corresponding to the formula Fe_2Si (20% Si) is neither a compd. nor a satd. solid soln. At room temp., the compd. Fe_2Si_2 dissolves in iron up to 16% of Si. The critical point of its solid soln. in iron gradually decreases from 790° to 450°, as the Si content increases from 0 to 16%. As the temp. rises, the soly. increases to 23% of Si at 1020°. By heating to above 1100°, the compd. Fe_2Si_2 dissociates into iron and FeSi. And in alloys contg. more than 23% of Si during cooling from the melt, FeSi primarily seps. from the melt, and at 1020° Fe_2Si_2 is formed from the compd. FeSi and iron. The change of the state of the constituents in the alloys, that is, dissoln. or sepn., formation or decompn. of the compds. in the alloys, has been conveniently studied by magnetic analysis. F. P. PHELPS

The delayed solution and the premature precipitation of cementite in eutectoid and hypereutectoid carbon steels. SAUVAGEOT *Compt. rend.* 173, 297–300(1921).—A microscopic study with ordinary C steels of the incomplete soln. and pptn. of cementite on passing A_c and A_r, resp. Cases are described for eutectoid and hypereutectoid steels which required 850–950° for complete soln. of cementite. Test pieces which were heated to 900°, slowly cooled to 725° and then quenched in water or oil showed about one-third of pptd. cementite. The temp. necessary for complete soln. of cementite is not always proportional to the C content but depends to a considerable extent on the initial condition of the Fe_3C. The spheroidal condition generally requires slightly higher temps. than that condition in which cementite exists as envelopes around the ferrite grains. W. A. MUDGE

An anomalous thermal expansion in hardened irreversible nickel steels. TOMIYA SUTOKI. *Sci. Reports Tohoku Imp. Univ. Japan* 10, 93–9(1921).—The anomalous expansion observable in hardened Ni steels is due to the tempering. On increasing the proportion of Ni in the steel the tempering temp. gradually increases from 330° to 400°. The $A_{1,3}$ point-concn. curve is much affected by the amt. of C present, the irreversibility increasing with the C. As to the formation of 2 kinds of martensite, it is very probable that during cooling β-martensite is first formed and then transformed into α-martensite, which is in turn changed into troostite. F. P. PHELPS

Remarks and observations concerning the phenomena in quenching steel. A. PORTEVIN AND P. CHEVENARD. *Rev. metal.* 18, 428–44(1921).—A general review and discussion, well illustrated with diagrams and photomicrographs, of the authors' investigations of the systems Fe–Fe_3C and Fe–Ni, the delayed soln. and premature pptn. of cementite, and the anomaly of dilatation in steels. The results disagree with Honda's conclusions (*C. A.* 13, 2850; 14, 2155, 3629). W. A. MUDGE

The nature of the transformations which occur on quenching steel. P. DEJEAN. *Rev. metal.* 18, 419–27(1921).—A further discussion of the two forms of martensite which are produced on quenching alloy steels, especially those of Ni (*C. A.* 11, 2882, and 14, 524), as influenced by recent results of Guillet [*C. A.* 15, 3064, 3065]. D. proposes to classify alloy steels in 3 groups: (1) the zone of austenite, (2) the martensitic or zone of stability, and (3) an intermediate zone of unstable equil. in which martensite is gradually changing to sorbite. W. A. MUDGE

Quenching tin-bearing brasses. LEON GUILLET. *Rev. metal.* 18, 445–58(1921); *Compt. rend.* 172, 1038–41(1921).—A study of the transformation points, microstructure, and effect of quenching on the physical properties of the 60:40, 70:30, and 80:20 brasses, in which the Zn has been replaced by 0.16–5.00% Sn. With the 60:40 brasses less than 0.85% Sn does not affect the crit. points; 1.00–3.00% Sn shows one abnormal

transformation point on heating at 480–90°, which disappears on cooling; more than 3.00% Sn shows two abnormal points, the temps. of which increase with the % of Sn. 1.6% Sn in the 70:30 brasses shows one point at 560° on heating and 540° on cooling. 3.00 Sn has no effect on the points of the 80:20 brasses. Less than 0.85% Sn has no effect on the microstructure of the 60:40 brasses; 0.85% Sn shows a trace of a new constituent, δ, similar to the δ in bronzes, which disappears on annealing for 2 hrs. at 800°; 1.00–5.00 Sn increases the amt. of δ proportionally. The 70:30 brasses show only a trace of δ with 3.6% Sn, and the 80:20 brasses show none for 3.00% Sn. The δ is due to the Sn and disappears on quenching as in the bronzes. Quenching brasses contg. insufficient Sn to form δ are identical with that for normal brasses. Complete physical data show the effect of annealing and quenching industrial 60:40 Sn brasses contg. 0.63–1.18% Sn and 1.7–2.7% Pb as cast, rolled and drawn. Less than 1.00% Sn increases tensile strength and hardness and reduces elongation to a slight extent but not sufficiently to cause difficulties in working. Quenching from 800° was detrimental; quenching from 600° improved the brasses contg. less than 1.00% Sn. The 70:30 brasses with 1.00% Sn were not improved by quenching. Those brasses with 1.18–2.00 % Sn are of little importance. W. A. Mudge

Transformation in metallic alloys. F. Hauser. *Z. Physik* **5**, 220–6(1921).—H. observes with a microscope a surface of Rose metal which is slowly cooled. Characteristic changes in appearance correspond to the freezing and transformation points. Photomicrographs are reproduced. F. C. Hoyt

Alloys of iron and uranium. E. P. Polushkin. *Iron and Steel Inst, Carnegie Schol. Mem.* **10**, 129 50(1920); cf. *C. A.* **15**, 48.—U-Fe alloys are pyrophoric. This property varies directly with the U content. Alloys contg. 16–18% are not pyrophoric even though they contain as much as 40% U. Alloys contg. 40–55% U and 0.7–3% C, and those contg. 85–90% U and 1.2–7.4% C are decomposed by water. V and Si apparently have no influence on the decompn. of the alloy by water unless the Si content is extremely high. Si then retards decompn. A polished sample placed on the emulsion of a photographic plate leaves an impression which after development by the usual process represents the structure of the specimen. The constituents that contain U can be identified by this method. In the manuf. of U steel the Fe-U alloy should be added in the ladle rather than in the furnace to secure max. recovery. Uranium oxide was present in all the samples of U steel examd. The following metallographic constituents were identified in Fe-U alloys: (1) UC etches gray in picric acid and becomes bluish after heat-tinting. Aqua regia reveals its cryst. structure. It is present in U steel. It does not go into solid soln. with Fe. (2) U_2C_3 is dark brown after heat-tinting and decomposes in water. (3) $Fe_3C.U_2C_3$ etches gray in picric acid and becomes blue-gray after heat-tinting. It resists etching even with aqua regia. Sodium picrate colors it dark brown. It is strongly radioactive, is harder than other U constituents, and is not decomposed by water. It is the principal constituent in alloys containing > 33% U and > 4% C. (4) A double uranium carbide is found rarely, and then only in alloys low in C. (5) V_2C occurs as very hard brilliant grains usually partly removed by polishing. Heat-tinting does not change its color. No common etching reagent colors or dissolves it. (6) Fe_6U occurs in alloys low in C and high in U. It etches gray in relief in picric acid and after heat-tinting becomes colored a yellow-brown lighter than ferrite. It is harder than ferrite. It is dissolved and colored violet by aqua regia and yellow or green by sodium picrate. (7) U is present in the free state in those alloys high in U in which the C is entirely combined with U and V and the Fe is combined with U and Si. It etches gray in picric acid. (8) FeSi occurs as a white brittle constituent usually full of cracks. It is not colored by heat-tinting. It dissolves in HF. (9) U_2C_3 is found as small sepd. occlusions in all alloys and in U steel. Ferrite and pearlite when present

have their usual appearance. Pearlite containing U seems darker than normal pearlite. Primary graphite has a regular shape, sometimes forming rays. Secondary graphite has no regular shape. Neither U nor any of its above mentioned compds. form solid solns. with Fe. V has greater affinity than U for C. F. P. FLAGG

Permeability of iron-vanadium alloys. R. DIETERLE. *Arch. Elektrotech.* **9**, 314–8(1920); *Science Abstracts* **24B**, 243–4.—The specimens tested were ellipsoids 22 cm. long and 0.4 cm. thick; they contained 0.61, 1.75, and 3.60% of V, resp. The material was heated at 850° for 2 hrs., cooled slowly, and then shaped into ellipsoids (state *A*). Hysteresis cycles were then taken, with max. fields of 30 and 80 gauss. The specimens were next heated for 1 hr. at 800° in N and slowly cooled (state *B*). They were magnetically examd. as before, and, after being heated to 900°, were plunged into water (state *C*). They were finally heated for 1 hr. at 900° and slowly cooled, to find whether the effect of the tempering could be removed. Tables are given for the 3 ellipsoids in the states denoted by *A*, *B*, and *C*. In state *A*, No. 1 bar was magnetically softest; No. 2 had the greatest max. and remanent induction; and No. 3 lay between these two. The annealing (*B*) improved all 3 alloys; No. 1 was again the softest; No. 2 had the highest μ max., *B* max., and *B* remanent; No. 3 exhibited least change. As the result of tempering (*C*), only No. 1 was substantially hardened. Metallographic observations confirmed these results. The part played by V is to assist in removing gases which tend to lower the magnetic quality; V combines readily with C and O, and thus acts as a deoxidizer and gas remover, and when present in larger amt. prevents the hardening which would be caused by C. The effect of V is similar to that of Si and Al. H. G.

Alloying tellurium with some white metals. J. H. RANSOM AND C. O. THIEME. *Chem. Met. Eng.* **25**, 102–3(1921).—Molten Pb and molten Sn dissolve Te; molten Zn and molten Al do not. Pb-Te and Sn-Te alloys are harder and stronger than pure Pb and pure Sn. Although Zn and Al do not dissolve Te the strength of both is increased by treating the molten metal with Te. A polished section of a Sn-Te alloy etched by 10% HNO_3 showed a large number of small white particles (probably a tin telluride) in a matrix of Sn crystals. The hardness of a Pb-Mg alloy containing 0.5% Mg was not changed by treatment with Te. The Te probably volatilized as magnesium telluride. F. P. FLAGG

High-resistance light alloys. LT. COL. GRARD. *Rev. metal.* **17**, 286–302(1920).—A study of the mechanical properties of two Al alloys contg., resp.: Cu 3.5–4, Mg 0.5, Mn 0.5–1% and Cu 2.5–3, Zn 1.5–3, Mg 0.5, Mn 0.5–1%, subjected to various heat and work treatments. S. L. C.

Experimental study of the heat treatment of metal pieces in the reverberatory furnace. M. FELIX VERDEAUX. *Rev. metal.* **17**, 312–34(1920).—A technical discussion of practical methods. S. L. C.

Corrosion, season cracking, decay of metals. E. G. JARVIS. *Brass World* **17**, 220–1(1921).—Decay is caused by allotropy and the movement of gases dissolved in metal, while season cracking may be due to severe cold working, NH_3 or other chemical (Hg salt or $FeCl_3$), superficial corrosion or internal stresses producing open cleavages in the grains. Corrosion may be chem., due to the simultaneous action of atm. and corrosive liquids, or due to electrochem. action. Corrosion may stop of itself by the production of protective compds. hindering further action. W. H. BOYNTON

The reduction of radiographic exposures (LEVY, WEST) **3**. The electrolytically produced calcium-barium-lead alloys comprizing Frary metal (COWAN, *et al.*) **4**.

Ore flotation. R. LUCKENBACH. U. S. 1,386,716, Aug. 9. An alk. soln. such as

is formed from shellac, alc., NaOH soln. and rosin or copal, NH_3 and H_2O is mixed with an aq. pulp of an ore and the mixt. is aerated to form bubbles and effect flotation sepn. Oleic acid also may be used. Cf. *C. A.* **15**, 1129.

Cyanide treatment of ores. L. D. MILLS and T. B. CROWE. U. S. 1,387,289, Aug. 9. In the cyanide treatment of ores or similar material, H_2SO_4 or other acid is added to the metal cyanide soln. to form HCN, air is passed through the soln. and the gas and vapor evolved are passed under suction over and through an alk. absorbent such as lime water, to effect recovery of cyanide.

Separating solutions from ore pulps. L. D. MILLS. U. S. 1,385,701, July 26. Ore pulp associated with cyanide soln. is allowed to stratify into a bottom layer of thick pulp, a middle layer of thin pulp and an upper layer of clear soln. The latter is drawn off to recover values from it and a fresh mixt. of pulp and soln. to be sepd. is fed to the settling tank. Thick pulp which has settled out is treated with a washing soln. to recover residual values from it, the washing soln. being of substantially the same sp. gr. as the pulp in order to prevent channeling, which would interfere with the success of the washing. A thickener of the Dorr type may be used in effecting the sepn.

Treating lead bullion. G. P. HULST and M. W. KREJCI. U. S. 1,386,503, Aug. 2. A bath of molten Pb bullion is agitated and at the same time treated, under non-oxidizing conditions, with a reagent such as S and PbO to effect sepn. of impurities in the form of a dross.

Open-hearth steel. L. B. LINDEMUTH. U. S. 1,385,562, July 26. Open-hearth steel is made by producing a "synthetic pig metal" from scrap in a melting furnace, removing S and charging the pig metal into an open-hearth furnace for finishing.

Iron and tin from tin scrap. P. A. MACKAY. U. S. 1,387,443, Aug. 9. Sn scrap is repeatedly dipped for short times in H_2SO_4 contg. free SO_3 in soln., the sepd. Fe is washed in H_2O and the oxidized Sn is recovered from the acid soln. and H_2O.

Alloy steel for electric heating elements. P. A. E. ARMSTRONG. U. S. 1,385,740, July 26. Elec. heating elements are formed of alloy steel contg. Cr about 20%, Si about 2%, Co about 2%, and C not over about 1.5%, the remainder being Fe.

Ferro-chrome alloy. W. B. BALLANTINE. U. S. 1,386,981, Aug. 9. See Brit. 159,568 (*C. A.* **15**, 2060).

Melting small pieces of metal. J. W. BASS. U. S. 1,386,226, Aug. 2. Borings, turnings or other small pieces of metal are spread in bulk along the bottom of a furnace and the upper portion of the mass is heated to form a crust over the entire upper surface. Products of combustion are caused to flow from one end of the mass over its upper side and portions of the metal are successively agitated in the direction of flow of the combustion products from one end of the material to the other.

Coated metal for torsion-springs. A. R. BECKERT. U. S. 1,386,834, Aug. 9. Torsion springs adapted to serve also as elec. conductors, *e. g.*, in elec. measuring app., are formed of a thin casing of highly resilient material such as phosphor bronze and an inner core of highly conducting material such as Cu.

Soldering aluminium. M. M. MERRITT. U. S. 1,387,426, Aug. 9. Al surfaces are prepd. for soldering by treatment with a soln. contg. HCl and electroplating with Cu.

Welding composition. W. R. CHAPIN. U. S. 1,387,351, Aug. 9. A mixt. for use in welding low-C Fe or steel to stellite or high speed steel is formed of ferro-Si 60, powdered Fe 20 and borax 20 parts.

10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

Halogenated nitrobenzaldehydes and halogenated indigos. L. C. JANSE. Univ. Leyden. *Rec. trav. chim.* **40**, 285–317(1921).—In BzH the CHO group reacts easily. In substituted derivs. of BzH the reactivity of the CHO group is changed. J. has begun a study of these effects. J. obtained the 3,5-Br_2 deriv. of 4-$H_2NC_6H_4CHO$ from the com. prepn. and into this deriv. Br, H, Cl and I were introduced, giving various halogen derivs. of BzH which on nitration gave *o*-NO_2 derivs. The constitution of these was proved by converting them into the corresponding benzoic acids and the halogen indigos. *Derivatives of p-$H_2NC_6H_4CHO$.* A technical prepn. of *p*-$H_2NC_6H_4CHO$ (A) was used. 4 g. A with 750 cc. H_2O + 10 cc. HCl (d. 1.05) was dissolved nearly completely at 70° and filtered. From this soln. the HCl salt seps. as a dark ppt. The soln. made alk. seps. A on cooling as a bright yellow substance. When Et_2O is added to this suspension A is dissolved; in drying with Na_2SO_4 some of the red-brown insol. form of A seps. The Et_2O soln. on evapn. gives A as a colorless cryst. residue, m. 71°. On exposure to air or in aq. soln. A is again transformed into the insol. yellow-brown form. The previously known azine, phenylhydrazone and oxime of A were prepd. 2 g. A in 350 cc. hot H_2O with 3 cc. HCl (d. 1.05) treated with 1.5 g. $NH_2CONHNH_2.HCl$ in 20 cc. hot H_2O and boiled 0.5 hr. sepd. on alkalinizing the cold soln. the semicarbazone of A, yellow platelets from H_2O, m. 173° (decompn.), which contain 0.5 mol. of H_2O. Four authors have described the prepn. of *p*-AcNHC$_6$H$_4$CHO (B) and all give a different m. p. for it. J. repeated the prepn. according to Blanksma (*C. A.* **5**, 1094). The Et_2O soln. of B was dried for 24 hrs. with Na_2SO_4 and in this way the formation of brown flocks on adding Ac_2O was avoided. The m. p. 153° was the same as that obtained by B. The azines, phenylhydrazones, oximes and semicarbazones described in this paper were obtained by boiling the aldehyde with the calcd. amt. of the proper N compd. *4,4'-Diacetoaminobenzalazine*, ($N:CHC_6H_4NHAc)_2$, seps. as yellow needles, m. 309–10° (decompn.); it differs from other azines here described in being sol. in EtOH. The phenylhydrazone of B seps. as long reddish yellow crystals, m. 209°, which redden rapidly in sunlight but do not change back in the dark. The oxime of B m. 205–6°. The *semicarbazone* of B seps. as yellow needles, m. 214°, which contain 1 H_2O of crystn. 3,5,4-$Br_2(H_2N)$-C_6H_2CHO (C) was previously prepd. by Blanksma (*l. c.*). 4 g. of the insol. form of A were boiled with 1.5 l. H_2O + 10 cc. HCl (d. 1.05) and filtered. At 25° 3.2 g. Br in 1.5 l. H_2O were added and the brown flocks of C sepd. as soon as possible by filtration. The bromination takes place well in glacial AcOH. The crude C was dissolved in a little hot EtOH and on pouring into H_2O C sepd. as white flocks, m. 150°. C undergoes decompn. when distd. *in vacuo*. *3,3',5,5'-Tetrabromo-4,4'-diaminobenzalazine* of C contains no H_2O of crystn. The *phenylhydrazone* of C is bright yellow, m. 147°, and becomes brown in light. The *oxime* seps. as colorless needles, m. 164°, and is obtained more slowly than similar derivs. of A and B. The *semicarbazone* of C seps. as yellow needles, m. 294°, which contain no H_2O of crystn. *Halogen derivatives of BzH.* 3,4,5-$Br_3C_6H_2CHO$ (D) was obtained by Blanksma (*C. A.* **7**, 769) from 3,5,4-$Br_2(H_2N)C_6H_2$-CHO (E). 5 g. E in EtOH were dispersed in H_2O and treated with 25 cc. 48% HBr and 50 cc. H_2O. E was not completely dissolved but 2.5 g. $NaNO_2$ in 27 cc. H_2O (ice cooled) was added until the starch-KI reaction was obtained. The mixt. was then poured into 4.5 g. $CuBr_2$ in 50 cc. 48% HBr and heated on the H_2O bath for 2 hrs. at 60–80°. When much dild. this mixt. sepd. 3.7 g. of D, m. 109°. *3,3',4,4',5,5'-Hexabromobenzalazine* of D seps. as clear yellow needles, m. 315°, with 2 H_2O of crystn., which is not lost by heating 7 hrs. at 130°. Only 3 other azines containing H_2O are known. The *phenylhydrazone* of D seps. as bright yellow leaves, m. 158°, becomes dark yellow

in sunlight. The *oxime* seps. as colorless needles, m. 172°. The *semicarbazone* gives small white needles, m. 314°; 3,5-$Br_2C_6H_3CHO$ (F) was obtained according to Blanksma (*C. A.* **5**, 1094). *3,3',5,5'-Tetrabromobenzalazine* sepd. as small yellow needles, m. 259°, containing no H_2O. The *phenylhydrazone* seps. as small colorless needles, m. 122°, which color slightly brown in the light, the color being permanent in the dark. The *oxime* seps. as small white needles, m. 123°. The *semicarbazone* gives white needles, m. 238°. *3,5-Dibromo-4-chlorobenzaldehyde* (G), obtained from E by using 38% HCl instead of HBr as in the prepn. of D, needles, m. 107°. 0.5 g. G heated under a condenser with 1 g. $KMnO_4$ in 100 cc. H_2O until G had disappeared was freed from $KMnO_4$ with EtOH and the MnO_2 was filtered off. The filtrate coned. and acidified with HCl sepd. *3,5-dibromo-4-chlorobenzoic acid*, long colorless needles from H_2O and EtOH, m. 235° (with sublimation). *3,5-Dibromo-4-iodobenzaldehyde* (H) was obtained from E. 8 g. E was dispersed in H_2O as described above and dissolved at 50° in 100 cc. glacial AcOH + 15 cc. coned. H_2SO_4. After adding 20 cc. H_2O the mixt. was cooled to 0° and diazotized with 4 g. $NaNO_2$ in 12 cc. H_2O. This mixt. was poured into a 3-l. flask containing 25 g. KI in 15 cc. H_2O. After 2 hrs. the mixt. was heated at 50–60° under a condenser until no more gas was evolved. $NaHSO_3$ was added to remove the I_2 and the brown crystals of H sepd. from the brown soln. The product was distd. with steam, treated with $NaHSO_3$ again and gave colorless needles from EtOH, m. 99°; this is a mixt. The residue in the flask was sepd., extd. with boiling EtOH and sepd. 1.9 g. H, m. 131°. *Halogenated nitrobenzaldehydes. 3,4,5-Tribromo-2-nitrobenzaldehyde* (I) was obtained by nitrating D either in a mixt. of equal parts of coned. H_2SO_4 and HNO_3 (d. 1.49) or with abs. HNO_3. 10 cc. H_2SO_4 + 10 cc. HNO_3 cooled to 12° were treated gradually with 1 g. D. When D had dissolved the mixt. was heated at 45° for 15 mins. and poured into crushed ice in which I sepd. as colorless crystals, m. 154°. *3,3',4,4'-5,5'-Hexabromo-2,2'-dinitrobenzalazine* seps. as yellow needles, m. 309° (decompn.). The *phenylhydrazone* of I m. 218° (decompn.); the EtOH soln. gives in the light a yellow ppt. which becomes red. The *oxime* of I seps. as colorless needles, m. 171°; dried at 110° for 2.5 hrs. the *anhydrous oxime*, m. 169°, is obtained. The *semicarbazone* of I seps. as colorless needles, m. 205°. I oxidized with excess $KMnO_4$ by boiling gave *3,4,5-tribromo-2-nitrobenzoic acid* as white needles, blackens 240°, m. slowly and becomes liquid at 264°. 1 g. I dissolved in 300 cc. dry C_6H_6 was exposed to sunlight in a sealed tube for 5 days and sepd. red crystals and a brown amorphous substance. The red crystals (m. 167°) were little sol. in H_2O and were sepd. from the brown substance (m. 196°), in this way showing that 2 products are formed. 1 g. I in 20 cc. Me_2CO isolated 15 days became red, then green and on evapn. gave a residue sol. in satd. Na_2CO_3. After filtering and adding HCl brown *3,4,5-tribromo-2-nitrosobenzoic acid* seps., m. 196°, identical with the brown substance obtained in C_6H_6 above. *3,5-Dibromo-2-nitrobenzaldehyde* (J) was obtained by nitrating F as in the prepn. of I from D; colorless needles, m. 133°. In the above nitration but one NO_2 group was introduced in the position 4, 2 or 6. It was shown that the NO_2 group in J is in position 2 by oxidizing the product with $KMnO_4$, which gave the corresponding benzoic acid. This acid is identical with the benzoic acid obtained on oxidizing 3,5,2-$Br_2(O_2N)C_6H_2Me$. *3,5-Dibromo-4-nitrobenzaldehyde* (K) was obtained in small amts. in the above nitrations of F, colorless needles, m. 166°, differs from J in its smaller soly. in 80% EtOH, by which it is sepd. from J by crystn. The constitution of K was detd. by the fact that with NaOH it does not give a halogenated indigo. *3,3',5,5'-Tetrabromo-2,2'-dinitrobenzalazine* seps. as yellow needles, m. 286°, sol. in $PhCH_2OAc$ and C_5H_5N but insol. in ordinary solvents. The *phenylhydrazone* of K seps. as dark red needles, m. 190°, gives in EtOH in sunlight a yellow ppt. that changes to red. The *oxime* of K was obtained with difficulty as crystals, m. 102°. The *semicarbazone* of K seps. as bright yellow needles, m.

236° (decompn.). 1 g. **K** in 15 cc. Me_2CO was exposed to sunlight 20 days and gave finally brown *3,5-dibromo-2-nitrosobenzoic acid*, blackens 172°, m. 209°. Nitration of **G** as above gave *3,5-dibromo-4-chloro-2-nitrobenzaldehyde* (**L**) as colorless needles, m. 125°, in almost quant. yield. Although it is possible for the NO_2 group to enter only in the *o*-position to the CHO group the fact that **L** with Me_2CO and NaOH gives *5,5'-7,7'-tetrabromo-6,6'-dichloroindigo* (**M**) is proof of its constitution since this only occurs when NO_2 and CHO are *o*- to each other. Nitration of **H** as above gave *3,5-dibromo-4-iodo-2-nitrobenzaldehyde* (**N**) as white needles, m. 186°. *Halogenated indigos.* In the preceding the prepn. of some halogenated nitrobenzaldehydes was described in which the NO_2 and halogen atom are *o*- to each other. By treatment with Me_2CO and NaOH these compds. give rise to halogenated indigos (Baeyer, Drewsen, *Ber.* **15**, 775, 781 (1882)), many of which have been prepd. by various workers. Thus 0.25 g. **J** in 4 cc. Me_2CO gives a red soln. to which 2 cc. 0.1 *N* NaOH was added drop by drop and the color was changed to a deep blue. The soln. was dild. in 1.5 l. H_2O and treated with 250 cc. 0.1 *N* NaOH which in 24 hrs. pptd. 5,5',7,7'-tetrabromoindigo (Grandmougin, *C. A.* **4**, 585), which crystd. from $PhNO_2$ as needles with a Cu luster. 0.25 g. **I** treated similarly gave a deep violet soln. from which 0.2 g. *5,5',6,6',7,7'-hexabromoindigo* was isolated as a blue powder and needles with a Cu luster from $PhNO_2$. **L** treated in this way gave **M** as stated above as a blue powder with a reddish tint. **N** treated in this way gave *5,5',7,7'-tetrabromo-6,6'-diiodoindigo* as a blue powder with a green tint.

E. J. WITZEMANN

The transformations of Hofman and of Curtius in their relation to steric hindrance. H. L. BUNING. Univ. Leyden. *Rec. trav. chim.* 40, 327–53(1921).—That substituents on the C_6H_4 ring may exercise a great influence on the course of reactions of aromatic compds. and that this influence may become a hindrance dependent upon the nature and position of the substituent has long been known. The sapon. of substituted benzamides is also subject to these influences. From the formula of an amide $\underset{(1)}{R}—\underset{(2)}{C}(:O)—\underset{(3)}{N}—H_2$ one has the impression that by the introduction of 2 *o*-substituents in the C_6H_4 ring R the bond (2) will become very energetic. The Hofmann reaction is one in which (1) and (2) play an important role and their behavior is represented by the following scheme: $RCONH_2 \longrightarrow RCONHBr \longrightarrow RC(ONa):NBr \longrightarrow [RCONNaBr] \longrightarrow RN:CO \longrightarrow RNH_2$. Do the bonds (1) and (3) become more solid when 2 *o*-substituents are introduced into the Ph group? If this is true the H. reaction would fail for di-*o*-substituted benzamides. Graebe and Rostowzew (*Ber.* **34**, 2111(1901)) have applied H.'s reaction successfully to $Cl_3(H_2NOC)C_6HCO_2H$, which gives 3,5,6,2-$Cl_3(H_2N)C_6HCO_2H$. The corresponding $Cl_4(H_2NOC)C_6CO_2H$ gives $Cl_4(H_2N)C_6CO_2H$ (Villiger and Blangey, *C. A.* **4**, 182; Reich, Salzmann and Kawa, *C. A.* **12**, 580). B. has now applied H.'s reaction to 2,4,6-$Br_3C_6H_2CONH_2$ (**A**), 2,5-$Br_2C_6H_3CONH_2$ (**B**) and 4,2,6-$MeBr_2C_6H_2CONH_2$ (**C**), and easily obtained, on treating them with Br in alkali, the corresponding anilines. This shows that 2 *o*-substituents merely make bond (2) stronger but produce no observable reinforcement of (1) or (3). The reaction of Curtius by which azides, $\underset{(1)}{R}—\underset{(2)}{C}(:O)—\underset{(3)}{N}\!\!<\!\!\begin{matrix}N\\ \|\\ N\end{matrix}$ are converted by boiling in H_2O into amines with one C atom less by the resolution of the bonds (1) and (3) is strictly analogous to H.'s reaction. Instances of the application of this reaction to azides of di-*o*-substituted BzOH are not known and so in order to exam. the inhibiting influence of 2 *o*-substituents B. has applied the C. reaction to the hydrazides corresponding to **A**, **B** and **C**. These were converted into the corresponding azides by HNO_2, which in turn converted them into the anilines at 0°. Here the bond (1) is not strengthened by the introduction of 2 *o*-Br atoms. The

bond (3) is considerably weakened so that although BzN_3 is stable the substituted azides examd. decomp. even at 0°. The above hydrazides were like the corresponding amides, very stable toward acids and alkalies. The above shows that the introduction of 2 *o*-substituents in amides, azides and hydrazides of BzOH produce alternately a weakening and strengthening of the bonds in the part of the mol. which is bound to the Ph ring. A number of instances of a weakening of the bond between the di-*o*-substituted ring and the rest of the mol. are known and are reviewed here. In all these cases the law of V. Meyer is often verified but his hypothesis is not. From these cases it might appear that the hindrance disappears when a few C atoms are inserted between the C_6H_5 ring and the CO_2H group. But this is not generally true. B. has found that 2,4,6-$Br_3C_6H_2CONHNH_2$ (D) is obtained from the $Cl_3C_6H_2COCl$ in Et_2O + excess N_2H_4 in H_2O but the dihydrazide is not formed, which shows that the NH_2 group in D is not influenced by $Cl_3C_6H_2COCl$. The $Cl_3C_6H_2COCl$, however, reacts well with unsubstituted $BzNHNH_2$. The corresponding derivs. of 2,6-$Br_2C_6H_3CO_2H$ and 4,2,6-Me-$Br_2C_6H_2CO_2H$ behave similarly, showing that the reaction of the NH_2 group is hindered by the presence of 2 *o*-Br atoms. Qual. expts. gave the following results: $BzNH-NH_2 + BzCl \longrightarrow BzNHNHBz + HCl$ very rapidly; using 2,4,6-$C_6H_2Br_3$ in place of Ph in both reagents in successive expts. the reaction is retarded in both cases but more so when the $Br_3C_6H_2COCl$ is used, although 2,4,6-$Br_3C_6H_2CONHNHBz$ is formed. If the 2,4,6-$C_6H_2Br_3$ group is used in both reagents only a 25% conversion into $(Br_3C_6H_2CONH)_2$ was obtained after boiling 5 hrs. Representing the mols. thus: $\overset{(1)}{C_6H_2Br_3}\overset{(2)}{—CO—Cl}$ and $\overset{(1)}{C_6H_2Br_2}\overset{(2)}{—CO}\overset{(3)}{—NH}\overset{(4)}{—N—H_2}$ one has the impression that by the introduction of 2 *o*-substituents the bonds (2) in the chloride and (4) for the hydrazide have become weakened. In order to answer the question as to how these phenomena observed in intermol. reactions may be related to the intromol. reactions of H. and C. B. enters into a critical historical study of the mechanism of intramol. reactions in which he develops the analogy existing between the 2 groups and shows how it is superfluous to make special hypotheses in order to explain intramol. transpositions. The laws controlling these phenomena will be detd. through additional data obtained from well chosen expts. Montagne's rule (*C. A.* **13**, 730) concerning the displacement of the Ph group was definitely confirmed for the 2,6-$Br_2C_6H_3$ and 4,2,6-$MeBr_2C_6H_2$ groups. Full details and references concerning the prepn. of the 2,4,6-tribromo-, 2,6-dibromo- and 4-methyl-2,6-dibromobenzonitriles from the corresponding anilines and their conversion into **A**, **B** and **C** are given. These 3 amides were all converted into the corresponding anilines as follows: 3 g. of finely powdered amide was placed in a soln. of NaOBr (3 g. NaOH + 2 g. atoms of Br for the amide used in 60 cc. H_2O) and dissolved rapidly. On heating on the H_2O bath the clear liquid became turbid and the nearly colorless aniline sepd. After cooling the aniline was sepd. washed, distd. with steam and recrystd. from EtOH and identified by its m. p. alone and when mixed with the same aniline from another source. The above amides **A**, **B** and **C** were sapond. (Bouveault, *Bull. soc. chim.* [3] 9, 370(1893)), the acids obtained transformed into the chlorides and these with a soln. of $NH_2NH_2.H_2O$ gave the 3 corresponding hydrazides *2,4,6-tribromobenzhydrazide*, (**E**), colorless needles from EtOH, m. 234° (decompn.); *2,6-dibromobenzhydrazide* (**F**), small needles, m. 204°; *4-methyl-2,6-dibromobenzhydrazide* (**G**), fine needles, m. 173°. 4 g. **E** and 3 g. each of **F** and **G** were separately dissolved in 15–30 cc. glacial AcOH. After cooling 1.2 cc. HCl (d. 1.19) was added and 0.75 g. $NaNO_2$ in 15 cc. H_2O. A white ppt. was formed and after 2 hrs. the corresponding anilines were sepd. by steam distn. and identified. Lorenzen (*J. prakt. Chem.* [2] **58**, 160(1898)) found that the esters of aromatic SO_2H acids are completely sapond. at room temp. by $NH_2NH_2.H_2O$. B. has found that *methyl 2,4,6-tribromobenzoate*, prismatic needles m. 69°, *methyl 2,6-dibromobenzoate*, spangles, m. 83°, and *methyl 4-methyl-2,6-dibromobenzoate*, needles, m.

48°, which are so difficultly sapond., are smoothly transformed, not into the hydrazides as might be expected by analogy with BzOEt, but into the free acids, which were isolated and identified. The above hydrazides react with aldehydes and ketones thus: $R'CONHNH_2 + OCR''R''' \longrightarrow R'CONHN:CR''R''' + H_2O$. The Me_2CO compds. were obtained by boiling 2 g. of the hydrazide with 20–50 cc. Me_2CO. The others were obtained by boiling 2 g. of the hydrazide in 30–40 cc. EtOH and adding 2 or 3 cc. BzH or MeCOPh or 15 cc. AcH. After boiling the products crystd. out on cooling: *ethylidene-2,4,6-tribromobenzhydrazide*, fine needles, m. 221°; *benzal-2,4,6-tribromobenzhydrazide*, brilliant needles, m. 224°; *isopropylidene-2,4,6 tribromobenzhydrazide*, brilliant needles, m. 221°; *α-phenylethylidene-2,4,6-tribromobenzhydrazide*, fine needles, m. 189°; *ethylidene-2,6-dibromobenzhydrazide*, spangles, m. 190°; *benzal-2,6-dibromobenzhydrazide*, grains, m. 201°; *isopropylidene-2,6-dibromobenzhydrazide*, grains, m. 230°; *α-phenylethylidene-2,6-dibromobenzhydrazide*, grains, m. 192°; *isopropylidene-[4-methyl-2,6-dibromobenz]hydrazide*, spangles, m. 239°; *α-phenylethylidene-[4-methyl-2,6-dibromobenz]-hydrazide*, spangles, m. 192°. E. J. WITZEMANN

Sulfonation in the presence of iodine. V. AUGER AND (MISS) M. VARV. *Compt. rend.* **173**, 239–40(1921).—Contrary to Ray and Dey (*C. A.* 15, 513), who claim to obtain only $o\text{-}HO_3SC_6H_4CO_2H$ (A) on sulfonating in the presence of I, sulfonation with 94%, 100% and fuming H_2SO_4 (20% SO_3) gave a mixt. of the 3 isomers in which only about 1% was **A**. This was detd. by heating the mixt. of SO_3H acids at 140° with an equal wt. of PhOH and several drops H_2SO_4 and comparing in alk. soln. the amt. of phenolsulfonephthalein formed with standards prepd. in the same way from known amts. of **A**. $m\text{-}HO_3SC_6H_4CONH_2$ m. 176°, not 170°. Contrary also to R. and D., who claimed formation of 4,1,2-$HO_3SC_6H_3(OH)_2$ in the presence of I, only the 3-isomer (**B**) and 3,4-$(HO_3S)_2$ acids are formed, the latter yielding a difficultly sol. Ba salt. With an excess of $Ba(OH)_2$ **B** forms a cryst. *basic barium salt*, $[C_6H_4(SO_3Ba)O_2]Ba.4H_2O$. It is concluded that I does *not* modify the course of sulfonations. M. H.

Artificial sweet materials. A. F. HOLLEMAN. Univ. Amsterdam. *Rec. trav. chim.* **40**, 446–50(1921).—The diamide of $o\text{-}C_6H_4(SO_3H)_2$ (A) has been described. The amide $o\text{-}HO_3CC_6H_4SO_2NH_2$ is spontaneously converted into saccharin by the loss of H_2O so that it seems probable that $o\text{-}C_6H_4(SO_2Cl)_2$ reacting with NH_3 would give *benzene-o-disulfonimide* (**B**), $C_6H_4:(SO_2)_2:NH$, also. Phthalimide, $o\text{-}C_6H_4:(CO)_2:NH$, is tasteless, while the substitution of a CO group with SO_2 gives sweet saccharin. The influence of 2 such substitutions giving **B** is unknown. Holleman and Polak (*C. A.* **5**, 680) described the prepn. of $o\text{-}C_6H_4(SO_3H)_2$ from $o\text{-}H_2NC_6H_4SO_3H$ (C) but H. could not obtain the good results described. H. proceeded thus: 86.5 g. C is placed in 1 l. H_2O containing 30 g. NaOH. A soln. of 37.5 g. $NaNO_2$ is added and the whole poured into 350 cc. 25% HCl in 1 l. H_2O. This liquor is neutralized, cooled to 0° and treated with 85 g. K xanthogenate in 250 cc. H_2O with agitation. The flask is now placed on the H_2O bath when N_2 is evolved and the ppt. usually formed is dissolved. The soln. is then filtered and evapd. *in vacuo*. The brown semisolid residue is extd. with EtOH until the salt residue is colorless. On evapg. the EtOH a brown viscous mass of crude xanthate remains. This is placed a little at a time in 400 cc. HNO_3 (d. 1.4) which becomes hot and evolves red fumes. When the oxidation is complete the HNO_3 is removed by coneg. *in vacuo*, adding H_2O and coneg. again 8 times in succession. The nearly neutral residue is dild. again in H_2O and freed from H_2SO_4 with a little $BaCl_2$ and then the Ba salt of $o\text{-}C_6H_4(SO_3H)_2$ is sepd. (yield 58.4%) by adding excess $BaCl_2$. This salt boiled with the calcd. amt. of Na_2SO_4 gives the Na salt, which with PCl_5 gives the chloride (**D**), $o\text{-}C_6H_4(SO_2Cl)_2$. 14.1 g. of the Na salt is triturated with 21 g. PCl_5, treated with 10 cc. $POCl_3$, heated under a condenser 4 hrs. at 130°, cooled and poured on crushed ice which sepd. **D**, m. 142°. 12 g. **D** in 220 cc. C_6H_6 treated with

agitation with 51 cc. of 3.42 *N* NH_3-EtOH seps. the so-called amide **A** mixed with NH_4Cl. The latter is sepd. by fractional crystn. with H_2O. The compd. obtained m. 254°, and is identical with that obtained by Armstrong and Napper (*Proc. Chem. Soc.* **16**, 160 (1900)). **A** has the compn. corresponding to $C_6H_4(SO_2NH_2)_2$ (**E**) but ought to be considered $C_6H_4:(SO_2)_2:NNH_4$ because its properties are entirely different from those of the *m*- and *p*-isomers of **E** and because **A** has a sweet taste (even at 1:1000 diln.) while the *m*- and *p*-isomers have no appreciable taste at this diln. When **A** is digested with the calcd. amt. of NaOH the *sodium salt* $C_6H_4:(SO_2)_2:NNa.H_2O$ is obtained. The *calcium salt* $[C_6H_4(SO_2)_2]_2Ca$ is obtained similarly and is also extremely sol. in H_2O. The 1% soln. is sweet and bitter in taste. The *free thiosaccharin* (**F**), $C_6H_4:(SO_2)_2:NH$, is obtained by digesting the NH_4 salt with the calcd. amt. of $Ba(OH)_2$ soln. to liberate the NH_3. The Ba is removed with H_2SO_4. On evapg. the filtrate *in vacuo* and finally in a desiccator over CaO **F** is obtained as hygroscopic crystals, m. 192°, soften at 186°, extremely sol. in H_2O, has at once a sweet and acid taste with a bitter after taste.

E. J. Witzemann

6-Aminopiperonal and its derivatives. Auguste Rilliet and Louis Kreitmann. Univ. Geneva. *Helvetica Chim. Acta* **4**, 588–99(1921).—A continuation of research on derivs. of 6-aminopiperonal (**A**) previously described (*C. A.* **8**, 659). 1 g. of **A**, 2 cc. of Me_2CO, 10 cc. of H_2O and a few drops of Na_2CO_3 heated at 100° until mineral acids no longer redden a drop of the mixt. and crystd. from dil. EtOH, yield *6,7-methylenedioxyquinaldine*, white needles, m. 150°, very sol. in EtOH, C_6H_6, less in petr. ether, cannot be steam distd.; *hydrochloride*, from EtOH-Et_2O mixt., small white needles; *chloromercurate*, long, colorless needles, m. 208°; *picrate*, from EtOH, small yellow needles, m. 182°; *chloroplatinate*, m. 261°; *methiodide*, from MeOH, white flakes, m. 273°. By a similar reaction and crystn. from dil. EtOH, was obtained *2,3-dimethyl-6,7-methylenedioxyquinoline*, long, colorless needles, m. 145°, b. 328–9°, volatile with steam, sol. in Me_2CO, petr. ether and Et_2O; *hydrochloride*, small white needles, decomp. without melting; *chloromercurate*, from H_2O, white needles, m. 282–4°; *picrate*, from EtOH, small yellow plates, m. 230°; *chloroplatinate*, from dil. HCl, long orange needles, m. 273°; *methiodide*, from EtOH, long pale yellow needles, m. 249–50°. *6,7-Methylenedioxy-α-phenylquinoline*, colorless plates with a pearly luster, m. 109°, very sol. in EtOH and C_6H_6, less in petr. ether; *hydrochloride*, brilliant light orange plates, m. 272°; *chloromercurate*, from H_2O, small white needles, m. 258–9°; *picrate*, from EtOH, yellow tufted needles, m. 195°; *chloroplatinate*, from dil. HCl, colorless plates, softening over a range of temp.; *methiodide*, yellow plates, m. 213° (decompn.).

C. C. Davis

Catechol. Karl Freudenberg. München. *Z. angew. Chem.* **34**, Aufsatzteil, 247–8(1921); *Collegium*, 1921, 284–8.—F. briefly summarizes the present knowledge of the chemistry of catechol. The identity of Kostanecki's methylated reduction product of catechol, the corresponding product from acacatechol and synthetic pentamethoxy-α,γ-diphenylpropane, on which doubt has been cast by Nierenstein, has now been further established by an absolute identity of m. p. and also by crystallographic measurements. The optical activity of the catechols is established, and it is shown that catechol and acacatechol are optical isomers, the former being *d*-catechol and the latter a mixt. of *l*- and *dl*-catechols. From acacatechol a *dl*-Ac compd. of high m. p. was isolated, and the same compd. was obtained by mixing together the Ac derivs. of catechol and acacatechol in the requisite proportions. It is suggested that the acacatechol originally present in acacia is pure *l*-catechol and that partial racemization occurs during extn. A similar partial racemization was observed during the prolonged boiling of an aq. soln. of *d*-catechol, and this is accompanied by the formation of a 2nd possible racemate, which was eventually isolated in a pure state by the transformation of the synthetically prepd. *dl*-catechol above mentioned.

C. J. West

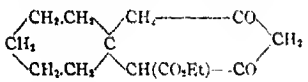
Course of the reduction of benzaldiacetyl monooxime and the preparation of benzyldiacetyl. OTTO DIELS AND WALTER PORTSCH. Univ. Kiel. *Ber.* **54B**, 1585–91 (1921).—When 20 g. PhCH:CHC(:NOH)COMe (A) in 400 cc. of 95% alc. is poured upon 10 g. of freshly activated Al and heated 2 hrs. on the H_2O bath under a reflux, filtered, the ppt. being extd. 4–5 times with boiling alc., and concd. on the H_2O bath there is obtained 15–6 g. of a dark red-brown viscous oil of pleasant odor which yields 2–3 g. of a mobile yellowish oil, b_3 105–10°, having an intense, very pleasant odor; a viscous yellow product, $b_{0.5}$ 200–15°, from which by extn. with boiling MeOH were isolated 2 cryst. substances but in too small amt. for thorough investigation; and a deep red-brown, feebly basic substance $b_{0.5}$ 260–70°. The first fraction consists chiefly of *1-phenyl-4-pentanone* (B), mobile liquid with an odor like that of Me hexyl ketone; *semicarbazone*, fine leaflets from MeOH, m. 125°. If 10 g. of B, 4 drops concd. HCl and 7.2 g. $AmNO_2$ are kept 20 min. at 50° and shaken 20 min. with 33% NaOH and the alk. soln. is freed from $AmNO_2$ with Et_2O and acidified in the cold with dil. H_2SO_4 it yields 1 g. $PhCH_2CH_2C(:NOH)COMe$ (C). A cold satd. soln. of A in alc. and 1–2% of colloidal Pd in a little H_2O shaken in H rapidly absorbs about 219 cc. H per g. A, when the reduction suddenly stops; if the soln. is now concd. on the H_2O bath, filtered, freed from the alc. as completely as possible and taken up in hot MeOH there seps. on cooling a *substance*, needles, m. 104°, mol. wt. in boiling C_6H_6 289–316, having the compn. $C_{22}H_{24}N_2$, which is apparently a pyrazine, $PhCH_2CH_2C(CMe:N)\!=\!N(CMe:CCH_2CH_2Ph)$. The MeOH mother liquors yield *benzyldiacetyl monooxime* (C), long faintly yellow prisms from ligroin or 50% AcOH, m. 94°, sol. in dil. alkalies with yellow color; *phenylhydrazone*, $C_{17}H_{19}ON_3$, fine, faintly yellowish needles, m. 149°. *Benzyldiacetyl dioxime* (2 g. from 2 g. C in a little MeOH and the calcd. amt. of NH_4OH in MeOH), leaflets from MeOH; 1 g. in dry Et_2O treated with 0.5 g. liquid NO_2, allowed to stand 15 min. in ice and 15 min. at room temp., washed with 20% NaOH and dried with $CaCl_2$ gives 1 g. of a *furoxan* $C_{11}H_{12}O_2N_2$, stout pearly crystals from MeOH, m. 63–4°. *Benzyldiacetyl* (3.5 g. from 5 g. C distd. with 200 g. of 35% H_2SO_4), deep yellow oil, b_{13} 128–9°. C. A. R.

New method of preparation of mellitic acid. ERNST PHILIPPI AND GERTRUU RIE. Univ. Vienna. *Monatsh.* **42**, 5–8(1921).—Diacetylmesitylene (*Ber.* **29**, 1413) may be reduced by Zn-Hg and HCl (*C. A.* **6**, 2919) to *diethylmesitylene* (A), $C_{12}H_{20}$, b. 229–36°. 15 g. of A, treated with 40 cc. AcCl and 50 g. $AlCl_3$ in 100 cc. CS_2, gave 17 g. *acetyldiethylmesitylene* (B), $C_{14}H_{22}O$, pale yellow oil, b. 286–304°. On further reduction, this yields *triethylmesitylene* (*1,3,5-trimethyl-2,4,6-triethylbenzene*), $C_{15}H_{24}$, b. 238–47°, with an odor of turpentine. On oxidation of B, by heating 2 g. in a sealed tube with a mixt. of 7 cc. HNO_3 and 2.5 cc. H_2O, 2 g. mellitic acid were obtained It may be purified through the Ba salt and then m. 285–6°. C. J. WEST

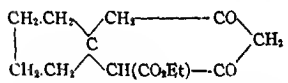
Unsaturated nature of the keto-enolic double bond. H. GAULT AND R. WEICK. *Compt. rend.* **173**, 315–8(1921); cf. *Compt. rend.* **170**, 1393; **171**, 395(1920).—Of the 3 forms of $PhCH_2COCO_2Et$ the liquid β-form (A), b_{15} 149°, was used. The remarkable ease with which this adds 2 atoms Br led to attempts to add other substances. HCl and HBr did not add, but caused isomerization into the α-form. HI caused hydrogenation. When NH_3 is passed into A at room temp. it soon solidifies, forming *phenylbenzylbutyrolactonecarboxamide*, $PhCH_2C(CONH_2).O.CO.CO.CHPh$ (B), m. 229°. In Et_2O at −15°, NH_3 produces initially a voluminous ppt. which loses NH_3 at a slightly higher temp. and liquefies. If this is filtered off in the cold and NH_3 again passed in, the same ppt. is again formed. After filtering this off and passing in NH_3 the *ammonium salt* of the enolic form of C (below) seps., while the filtrate from this, freed from the

excess of NH_3, deposits B and finally an oil which solidifies and is *ethyl phenylbenzylbutyrolactonecarboxylate*, $PhCH_2C(CO_2Et).O.CO.C(OH):CPh$ (C). Curiously, C functions as an acid while B does not. Et_2NH causes a similar bimol. cyclization. At room temp. in Et_2O it gives with A the *diethylamine salt* of C, m. 130–5° with evolution of Et_2NH. Even at −15° immediate lactonization results. M. HEIDELBERGER

Formation and stability of spiro compounds. V. Derivatives of cyclohexanespirocyclohexane and of cyclopentanespirocyclohexane. W. S. G. P. NORRIS AND J. THORPE. Imp. Inst. Sci. Tech., South Kensington. *J. Chem. Soc.* **119**, 1199–1210 (1921); cf. *C. A.* **15**, 2829.—This study was undertaken to obtain further information about spiro compds. and some insight into the nature of the valency as it occurs in C compds. by comparing the stability of spiran hydrocarbons. *Ethyl cyclohexanespirocyclohexane-3,5-dione-2-carboxylate* (I) was prepd. by condensing 46.5 g. $CH_2:(CH_2CH_2)_2:C:CHCOMe$ (Wallach, *C. A.* **7**, 1002, who, however, assigned another formula which N. and T. believe incorrect) with 48 g. $CH_2(CO_2Et)_2$ and 7.5 g. Na in 150 cc. alc., small needles from alc. or H_2O, containing 1 H_2O, m. 87° to a bright red liquid. It behaves as a monobasic acid; aq. or alc. $FeCl_3$ gives a reddish violet color. The anhydrous ester is a yellow, viscous gum. On hydrolysis by boiling with $Ba(OH)_2$ the acid loses CO_2, giving *cyclohexanespirocyclohexane-3,5-dione* (A), $CH_2(CH_2CH_2)_2C(CH_2CO)_2CH_2$, clusters of small needles, m. 170.5° to a brigbt red liquid. In the prepn. of this compd. it is not necessary to isolate the ester.



I



II

Anilide, $C_{17}H_{21}ON$, bright yellow needles, m. 162–5°. HCHO gives *methylenebiscyclohexanespirocyclohexane-3,5-dione*, $CH_2(C_2H_{10}:C[CH_2CO]_2CH)_2$, sbort needles, m. 206°. Oxidation of 5 g. A in 25 cc. 10% NaOH at 0° with 15.5 g. Br in 350 g. H_2O (neutralized witb 10% NaOH) gave a quant. yield of *cyclohexane-1,1-diacetic acid* (B), $CH_2(CH_2CH_2)_2C(CH_2CO_2H)_2$, m. 179°. With $KMnO_4$, *cyclohexane-1-acetic-1-carboxylic acid* is formed, $C_9H_{14}O_4$, prisms, m. 134°. *Silver salt. Anhydride*, by boiling tbe acid with AcCl for 1.5 hrs., glistening plates, m. 57°. *Anilic acid*, $C_{15}H_{19}O_3N$, from the anhydride and $PhNH_2$ in C_6H_6, glistening plates from alc., m. 180°. B forms a Ca salt, which is pptd. on boiling a neutral soln. of the NH_4 salt with $CaCl_2$. *Ethyl cyclopentanespirocyclohexane-3,5-dione-2-carboxylate* (II), was prepd. from $(CH_2CH_2)_2C:CHCOMe$ and $NaCH(CO_2Et)_2$, small plates with 1 H_2O, m. 65–7°. The anhydrous ester is a yellow oil. *Cyclopentanespirocyclohexane-3,5-dione* (C), by hydrolysis of II with $Ba(OH)_2$, needles m. 135–6.5°; the alc. soln. gives a reddish purple color with $FeCl_3$. *Anilide*, clusters of brigbt yellow needles from alc., m. 171°. *Methylene derivative*, $C_{11}H_{12}O_4$, flattened needles from alc., m. 165°. Upon oxidation with NaBrO, C gives *cyclopentane-1,1-diacetic acid*, m. 178–9°, and with $KMnO_4$ *cyclopentane-1-acetic-1-carboxylic acid*, sbort needles, m. 156.5°. B was synthesized by condensing $CH_2(CH_2CH_2)_2C:CHCO_2Et$ with $CNCHNaCO_2Et$ and hydrolyzing with aq. H_2SO_4. *Cyclohexanespiro-4-bromocyclohexane-3,5-dione* (D), $C_{11}H_{13}O_2Br$, by adding a sligbt excess of Br in $CHCl_3$ to A in $CHCl_3$, and purifying through the Na salt, needles, m. 177°. The *4,4-dibromo derivative* (E) was prepd. by grinding 2 g. A with 20 cc. H_2O containing 10 g. Br., long needles, m. 125°. E is almost quant. transformed into D by treating 1 g. with 20 cc. 10% NaOH containing an excess of $CO(NH_2)_2$. *4-Chloro derivative* (F), $C_{11}H_{13}O_2Cl$, by passing Cl gas into A in $CHCl_3$, needles witb 1 H_2O from alc., m. 166–5°. *4,4-Dichloro derivative* (G), a by-product of F, insol. in $NaHCO_3$, also obtained quant. by using a large excess

of Cl, needles, m. 89°. G is quant. transformed into F by treatment with KI in glacial AcOH. The *4-chloro-4-bromo derivative* may be prepd. either by treating D with Cl or F with Br, both operations in $CHCl_3$, and extg. the product with $NaHCO_3$, slender needles, m. 101°. *4-Chloro-4-bromo-1,1-dimethylcyclohexane-3,5-dione*, $C_8H_{10}O_2ClBr$, from the Br or Cl deriv. (Vorländer, *Ann.* 322, 239), long, felted needles, m. 138.5°. *Cyclopentanespiro-4-bromocyclohexane-3,5-dione*, $C_{10}H_{13}O_2Br$, flat plates, m. 157°. *4,4-Dibromo derivative*, needles from C_6H_6, m. 111°. VI. New derivatives of cyclopropane and cyclohexanespirocyclopropane. Stanley Francis Birch, William Henry and George Armand Robert Kon. *Ibid* 1315–28.—In searching for possible new sources of cyclopropane derivs. it has been found that the bridged piperidine compds. of Guareschi (*C. A.* 6, 865) on regulated hydrolysis with alkali furnish such a source. *2,3-Dicyano-1,1-dimethylcyclopropane-2-carboxamide* (H). $Me_2C\langle\begin{smallmatrix}CHCN\\|\\C(CN)CONH_2\end{smallmatrix}\rangle$ is obtained by boiling $Me_2C\langle\begin{smallmatrix}C(CN)CO\\|\\C(CN)CO\end{smallmatrix}\rangle NH$ with 10% KOH (1 mol.) for 5 min. and then cooling, long flattened needles from dil. alc. or C_6H_6, m. 163.5°. The *acid*, $C_8H_8O_3N_2$ (J), is obtained when 5 g. H in 100 cc. cold concd. H_2SO_4 are treated with satd. $NaNO_2$ in H_2O until the mixt. is nearly solid. The product is poured into H_2O, extd. with Et_2O and the acid removed with Na_2CO_3. It forms large transparent rhombic laminas, m. 168–9°, from H_2O. The acid may also be obtained by boiling the imide with 5% KOH for 1 hr. The mother-liquors from J contained terebic acid and a *compound*, $HOCMe_2CH(CN)CH(CN)CO_2H$ (?), forming fine, long needles from H_2O and m. 234–5°. J, heated with a little water in a sealed tube for 1 hr. at 180–200°, gave *1,1-dimethylcyclopropane-2,3-dinitrile*, $C_7H_8N_2$, b_{12} 158°, long, flattened needles, m. 50°. Boiled with alc. KOH, a mixt. of *cis*- and *trans*-caronic acids was obtained (Beesley, Ingold, and Thorpe, *C. A.* 9, 3059). When 3.8 g. H are heated with 6 g. KOH in 45 cc. H_2O for 3–4 hrs., *β-hydroxy-β-methylbutane-α,δ,δ-tricarboxylic lactone* (K), $C_8H_{10}O_6$, is formed, large prisms from a small amt. H_2O (in which it is very sol.), m. 157°. *Silver salt*, very sol. in H_2O. Warmed with 25% H_2SO_4, the lactone loses 1 CO_2 and gives terebic acid (*J. Chem. Soc.* 75, 48). *α,β-Dicyano-α-hydroxy-α-methylbutane-α,β-dicarboxylic acid* (L), $Me_2C(OH)C(CN)(CO_2H)CH(CN)CO_2H$, prepd. by heating the imide with 3 mols. aq. KOH for 0.5 hr. and then acidifying, thick, transparent rhombic plates from H_2O, m. 195–6° (decompn.). With 50% H_2SO_4 the acid is decompd. into $(HO_2CCH_2)_2$ and AcMe. The action of concd. KOH on the imide gave K. *Cyclohexanespiro-2,3-dicyanocyclopropane-2-carboxamide*, $C_{11}H_{11}ON_3$, from the spiro-imide as above, fine, glistening plates or felted needles from dil. alc. or C_6H_6, m. 141°. The *acid*, $C_{11}H_{12}O_2N_2$, prepd. by the action of $NaNO_2$ on the amide or by direct hydrolysis of the spiro-imide with 2 mols. KOH, forms prisms, m. 159°, best from 50% HCl. *Cyclohexanespirocyclopropane-2,3-dinitrile*, $C_{10}H_{12}N_2$, lustrous plates, m. 86°, which, on hydrolysis, gave cyclohexanespirocyclopropane-2,3-dicarboxylic acid (B., I. and T.) *1-Hydroxycyclohexylethane-α,β,β-tricarboxylic γ-lactone*, $C_{11}H_{14}O_6$ (M), by heating the amide with 15% KOH for 4 hrs., spherical aggregates of buff-colored crystals, m. (not sharply) 183–4°, which is probably the *trans*-isomer since it is not affected by boiling AcCl. *Silver salt*. On heating above the m. p., or on boiling with 20% H_2SO_4, the *α-lactone of the α,β-dicarboxylic acid* (N) is formed, plates from H_2O, m. 184–5°. *Silver salts*, both of the lactonic acid and the dibasic HO acid, were prepd. N is stable to $KMnO_4$. *Anilide*, $C_{18}H_{19}ON$, iridescent plates, m. 113°. In its formation 1 H_2O and 1 CO_2 appear to be eliminated. *Cyclohexanespirb-2,3-dicyanocyclopropane-2,3-dicarboxylic acid*, $C_{11}H_{12}O_4N_2$, by boiling a soln. of the spiro-imide in 3 mols. 10% KOH for 30–40 min., small

plates from dil. alc., m. and decomp. 207°. ***Ankydride,*** by heating above the m. p. of the acid for 20 min., colored crystals, m. 99°. When an excess of KOH is used in the hydrolysis, *cyclohexanespiro-2-cyanocyclopropane-2,3,3-tricarboxylic acid,* $C_{13}H_{13}O_6N$, results, stellate clusters of prisms, m. 169° (decompn.). The *potassium hydrogen salt* forms needles from alc., m. 237° (decompn.). C. J. West

A new case of anisotropy in the melting point. Arno Müller. Univ. Leipzig. *Ber.* **54B**, 1481–2(1921).—M. prepd. dianisal cyclohexanone, for which Wallach (*Terpene u. Campher* **1909**, p. 427) gives 159° as the m. p., from 1 g. freshly distd. cyclohexanone and 2.8 g. $MeOC_6H_4CHO$ (purified through the $NaHSO_3$ compd.) in 7.5 cc. alc. allowed to stand a day with 2 cc. of 8% NaOH and crystd. from 250 cc. alc., from which it seps. in yellow dichroitic needles, which liquefy completely 160–1° but the melt is turbid and on further slow heating clears sharply at 171°. Optical investigation shows that this is a case of anisotropy. Chas. A. Roulller

Action of ethylmagnesium bromide on dibenzylidenecyclohexanone and dibenzylidenemethylcyclohexanone. Manolesco. *Compt. rend.* **172**, 1360–2(1921).—The work of Kohler (*Am. Chem. J.* **36**, 177(1906); *C. A.* **1**, 1849) and Haller and Bauer (*Compt. rend.* **142**, 971(1906)) has shown that when the Grignard reagent interacts with benzylidene derivs. of β-methylcyclohexanone, camphor, etc., the organic radical is joined not to the ketonic group but to the C (of the benzylidene chain) in the α-position to the CO group. M. working on dibenzylidenecyclohexanone (A) hoped to obtain compds. similar to those obtained by K., and starting with A prepd. by the method of Petrenko-Kritschenko and Arzibascheff (*Ber.* **29**, 2052(1896)) and its *p*-Me deriv. treated these compds. in ether with MgEtBr, in attempting to secure either the mono-Et or the di-Et deriv. In the case of the 2 dibenzylidene compds. a cryst. product was obtained and an oil which is being investigated. The cryst. products correspond to the formulas $C_{28}H_{34}O_2$ and $C_{28}H_{36}O_2$, peroxides of the mono-Et compds. These liberate I from KI in AcOH. Powdered A was added in small amts. to MgEtBr in Et_2O and the reaction which started at once was completed on the water bath by heating the mixt. for 0.5 hr. Satd. NH_4Cl was added to decomp. the Mg compd. as it was found that dil. acid was not suitable for that purpose. On evapg. the ether soln. crystals, of the *compound* $C_{28}H_{34}O_2$ (B), m. 137.05°, were obtained. The yield was 25% and it rose to 55–60% when air was blown through the ether soln. When B was treated with KI in AcOH, I corresponding to one atom of O_2 was liberated and a compd., $C_{28}H_{34}O_2$, m. 111°, was formed. The action of BzCl on the ether soln. of the addition product formed by the action of MgEtBr on A was investigated, the mixt. being iced during the addition of BzCl and after warming the mixt. for 0.5 hr., crystals, m. 105°, corresponding to the formula $C_{21}H_{18}O_2$ were formed. They are sol. in ether and $CHCl_3$ and their

$$\begin{matrix} CH_2. & CH_2. & CH_2 \\ | & & | \end{matrix}$$

constitution is given as PhEtCHC: (COBz). C: CHPh. When the compd. was sapond. with alc. KOH, BzOK and an oil (C) were formed and alcoholysis led to the same results. When PhCH: CHCOCl was used in place of BzCl crystals, m. 122–3°, slightly sol. in ether, sol. in C_6H_6, were obtained and on sapon. cinnamic acid and C were formed. The *compound* $C_{21}H_{18}O_2$, m. 119–20°, was obtained in a similar way when *p*-methyldibenzylidenecyclohexanone was used. The product formed is very sol. in ether and in C_6H_6 and it shows the peroxide reaction. H. E. W.

Optical investigations in the chemistry of terpenes. I. Arno Müller. Leipzig. *Ber.* **54B**, 1466–71(1921); cf. Hantzsch, *C. A.* **6**, 1435.—The present paper describes the results of a systematic application of H.'s methods to citronellol (A), geraniol (B), nerol (C) and their functional derivs. The greatest care was taken in purifying the substances but it was found that the 3 alcs. and their acetates are much less sensitive

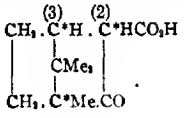
than has been assumed and that ordinary distn. under the conditions observed by H. suffices for their purification. The purification of the cyclo products and cyclo esters of the above alcs., however, is subject to the same difficulties observed by him with the more sensitive terpenes, although even in these cases the products are considerably less sensitive than the true terpenes. A isolated from Java oil of citronella absorbs somewhat more than the product obtained by reduction but the deviations are slight and show no material differences. B purified through the $CaCl_2$ compd. absorbs far less while the band for C lies between those for A and B but closer to that for B. The differences are more marked in the case of the acetates, prepd. from the alcs. with Ac_2O and NaOAc. The cyclo alcs., prepd. by treating the esters of A, B and C at a low temp. with H_3PO_4, repeatedly fractionating and hydrolyzing, show very similar absorption (possibly the bands would be identical if the alcs. were absolutely pure) while the esters of the cyclo B and C differ greatly (600 Angström units) from that of cyclo A. Dihydrocitronellol, hydrogenated reuniol and tetrahydrogeraniol show almost identical absorption. In view of previous chem. observations it may be concluded, from the spectrum of C, that it is a mixt. of about 40% A and 60% B while in the cyclo acetate the equil. is shifted in favor of B, owing to the fact that in the cyclization much A is destroyed. In the conversion of B into the acetate the absorption is shifted about 300 units towards the red, in that of A into its acetate about 500–600 units; the same is true of the cyclo compds. In passing from A and B to the cyclo alcs. the absorption is shifted 300–400 and 200–300 units, resp., towards the red. CHAS. A. ROUILLER

Benzalcarvone. ARNO MÜLLER. Leipzig. *Ber.* 54B, 1471–81(1921).—When 210 g. carvone, d_{15} 0.9642, $[\alpha]_D$ −59.48°, and 160 g. BzH in 560 cc. alc. are slowly treated with 200 cc. of 15% NaOH below 2–3°, the turbidity which soon appears being destroyed by addition of alc., then allowed to stand 8 hrs. at 0° and 48 hrs. at room temp. and poured into H_2O and the resulting oil is taken up in Et_2O, washed with H_2O and dil. tartaric acid to remove the alkali and dried with Na_2SO_4 there are obtained 300 g. crude product which under 10 mm. gives 52 g. h. below 100°, 26 g. b. 100–10°, 30 g. b. 110–70°, 82 g. b. 170–80° and 60 g. h. 180–225°. The fractions up to 110° contain chiefly the unchanged components and $PhCH_2OH$, those from 110–70° carvone and small amts. of the condensation product and the residue above 180° the amorphous substance obtained by Wallach in attempting to prep. benzalcarvone (*Ann.* 305, 274). Further fractionation under 13.5 mm. of 135 g. of the 170–225° product gave the following fractions, for which are given the rotation in a 100-mm. tube and the mol. wt. in AcOH: 202–5°, 30 5 g., 93.45°, 238.3; 205–8°, 29.2 g., 77.30°, 226.3; 208–10°, 31.6 g., 53.45°, 215.6; 210–5°, 20.3 g., 33.45°, 213.2; 215–27°, 18.2 g., −4.00°, 180.8; solid residue, 5.2 g., ——, 119.2. Another distn. of the 202–5° fraction gave liquid or *α-benzalcarvone* as a light yellow, almost odorless oil, b_{10} 195–7°, d_{15} 1.0520–1.0560, $[\alpha]_D$ 92.30–93.45°, difficultly volatile with steam, exceedingly viscous and shows no tendency to solidify even in the cold; on long standing it deposits crystals of an isomeric *β-benzalcarvone*, almost white leaflets from alc., m. 114–5°, mol. wt. in AcOH 238.2, α of a 1% alc. soln. in a 100 mm. tube −815°; both forms show red-orange and brick-yellow halochromism. The oil from which the *β*-form has sepd. now b_{10} 191–3° and shows d_{15} 1.041, $[\alpha]_D$ 152.30°, while the mol. wt. remains unchanged (244.5). The ultraviolet absorption of the *β*-form resembles that of benzalmenthone while that of the *α*-form is like the absorption of benzaldihydrocarvone. No oxime or semicarbazone could be obtained from either form. The *α*-form (5 g.) in 25 cc. Et_2O in ice (protected from moisture with P_2O_5) treated with dry HCl eagerly absorbs the gas; after 1 day in ice the dark soln. is washed with H_2O, dried with Na_2SO_4 and cautiously concd., giving 5.6 g. of a dark brown oil which on heating under atm. pressure evolves HCl abundantly; the *β*-form, on the other hand, does not react with HCl. Either form reduced in alc.

with 0.5 part Na gives benzyldihydrocarveol, identified through the *phenylurethan*, m. 233–4°, identical with the product, h_{11} 182–4°, obtained by reduction with Na of benzaldihydrocarvone, which in turn is obtained in 20% yield from 25 g. dihydrocarvone and 17 g. BzH in 200 cc. alc. allowed to stand 8 days in a cool place with 3.75 g. Na in 250 cc. alc. Both forms with $KMnO_4$ in Me_2CO give BzOH and a small amt. of an oil smelling like *p*-$MeOC_6H_4CHO$, which did not react with $H_2NCONHNH_2$. M. concludes that the β-form has the structure $CMe.CO.C:CHPh$ (‖) $CH.CH_2.CHCMe:CH_2$ while that of the α-form cannot yet be detd.

CHAS. A. ROUILLER.

The two *d*-methyl allylcamphocarboxylates, the three isopropyl camphocarboxylate lactones and the campho-2-propanol yielded by them. A. HALLER AND MLLE. RAMART-LUCAS. *Compt. rend.* 173, 115–20(1921).—The authors' researches led them to these conclusions: (1) In the prepn. of the *d*-Me alkylcamphocarboxylates there are formed two stereoisomers but not two enantiomorphs. In the case of the allyl deriv. each of the lactones, m. 141° and 117–8°, is characteristic, the first of the solid Me allylcamphocarboxylate and the second of its liquid isomer; (2) the formation of the lactone of the solid allylcamphocarboxylate (II) is conditioned either by the new asym. C atom which appears in the lateral chain and is independent of the three other asym. C atoms of the β-ketonic form of camphocarboxylic acid (I) or by the asym. 3-C atom; the formation



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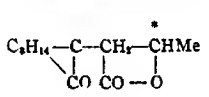
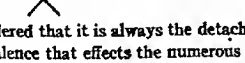


II

of the same camphopropanol from the two lactones, m. 141° and m. 117–8°, proves the mobility of the CO_2H group in the latter two compds.

R. L. BROWN

Transpositions of certain aromatic compounds. E. BAMBERGER. *J. prakt. Chem.* 102, 267–75(1921).—The mode of formation of Ph_2 derivs. led both B. (*Ber.* 28, 404(1895)) and Kühling (*Ber.* 28, 43(1895)) to assume that in their product, $O_2NC_6H_4C_6H_4Me$ (A), both NO_2 and Me groups were in the *p*-position. The work of Kliegel and Huber (*C. A.* 15, 843) in transforming A into a compd. they proved to be 4-hydroxy-2-methyldiphenyl has convinced B. that the structure of A is 4-nitro-2-methyldiphenyl (*C. A.* 15, 843). K. and H. in further work suppose an intermediate and momentary structure—PhNH—in the rearrangement of PhNHOH to $H_2NC_6H_4OH$, which corresponds to the hypothesis of Stieglitz, $\rangle C_6H_4{=}NH$ (*Am. Chem. J.* 29, 49(1903)). B. favors the hypothetical structure of S., and applies this to a number of reactions, *e. g.*, the formation of *p*-amino-*p'*-hydroxydiphenyl: $PhNHOH \longrightarrow HO\rangle C_6H_4{:}NH \longrightarrow HOC_6H_4\rangle C_6H_4{:}NH \longrightarrow HOC_6H_4C_6H_4NH_2$. In the same way the transformation of azoxy- into hydroxyazobenzene is assumed to be $PhN{:}N(:O)Ph \longrightarrow PhN{:}N(OH){:}C_6H_4< \longrightarrow PhN{:}NC_6H_4OH$ and of *o*-nitrosophenol $PhNO_2 \longrightarrow$



o-HOC_6H_4NO.

In general it is considered that it is always the detachment and migration of a H atom with resulting free valence that effects the numerous condensations and transpositions discussed.

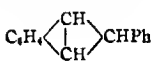
C. C. DAVIS

Hydrobenzoin and semipinacolin transpositions in the series of triarylglycols with *p*-methoxyl substitutions (anisylglycols). A. Orékoff and M. Tiffeneau. Boucicaut Hospital. *Bull. soc. chim.* **29**, 445–59(1921).—The general reactions involved have been discussed previously (*C. A.* **14**, 3643). 21 g. of benzoin heated 3 hrs. with 75 g. *p*-BrC_6H_4OMe (A) and 9.6 g. of Mg, acidified, cooled, dried, and washed with Et_2O, yield 23 g. of *p-anisyl-1-diphenyl-1,2-ethanediol* (B), cryst. powder, m. 197–8°, sparingly sol. in EtOH and C_6H_6, sol. in PhMe and hot HOAc, insol. in Et_2O, sol. in concd. H_2SO_4 with yellow-brown color. 20 g. of B boiled 3 hrs. with 200 cc. 50% H_2SO_4, extd. with Et_2O, washed with dil. NaOH, H_2O, dried with Na_2SO_4, and evapd., yield *anisyldesoxybenzoin* (C), small colorless crystals from warm EtOH, m. 88–9°, sol. in most solvents. *Oxime*, small colorless crystals from EtOH, m. 139–40°. The semicarbazone could not be prepd. 6 g. of C boiled 12 hrs. with 6 g. of KOH in 30 cc. of EtOH dild., extd., acidified, yield BzH and $PhCH_2OMe$ (*J. Chem. Soc.* **41**, 227). 16.6 g. of $PhCH(OH)CO_2Me$ heated 2 hrs. with 74.8 g. of A and 9.6 g. of Mg, acidified, dried and washed with Et_2O, yield 24 g. of *1,1-di-p-anisyl-2-phenylethanediol* (D), silky needles from hot PhMe, m. 197–8°, very sol. in xylene, hot HOAc, less sol. in PhMe, C_6H_6, EtOH, insol. in Et_2O, sol. in concd. H_2SO_4 with a red-violet color. 10 g. of D boiled 1.5 hrs. with 150 cc. 20% H_2SO_4, dild., extd. with Et_2O, dried with Na_2SO_4, distd., the oil shaken with cold MeOH and the ppt. dried, yield 8.5 g. of *1,1-di-p-anisyl-2-phenylethanone* (E), small brilliant needles from warm MeOH, m. 57–8°, very sol. in most solvents, less in cold MeOH and petr. ether, sol. in concd. H_2SO_4 with red-violet color. *Oxime*, needles from EtOH, m. 164–5°. The semicarbazone could not be prepd. 5 g. of E boiled 5 hrs. with 5 g. of KOH in 25 cc. of EtOH, dild., extd., acidified, yield BzOH and $(p\text{-}MeOC_6H_4)_2CH_2$ (*Ann.* 194, 323). 52.5 g. of $p\text{-}MeOC_6H_4CH(OH)CO_2Me$ heated 2 hrs. with 157 g. of PhBr and 24 g. of Mg in Et_2O, acidified, dried, washed with Et_2O, yield 73.5 g. of *1-p-anisyl-2,2-diphenyl-1,2-ethanediol* (F), white powder, m. 192–4°, sparingly sol. in EtOH and C_6H_6, more sol. in PhMe and hot HOAc, forms a yellow-green soln. in concd. H_2SO_4. 15 g. of F boiled with 150 cc. 50% H_2SO_4 2 hrs. and treated as before, yield *anisyldiphenylethanone*, small crystals, m. 88–9°. *Oxime*, m. 139–40°. The mother liquor after extn. with Et_2O, evapd. to an oil, excess NaOAc and alc. $ClH_3NCONHNH_2Cl$ added, boiled 15 hrs., dild., filtered and dried, yield the *semicarbazone* of *anisyldiphenylacetaldehyde* (G), small white crystals from MeOH, m. 198–9°. 5 g. of G boiled 2 hrs. with 125 cc. 50% H_2SO_4, extd. with Et_2O, yield *anisyldiphenylacetaldehyde* (H), needles from MeOH, m. 75–6°, sol. in most solvents. *Oxime*, m. 180–1°. 5 g. of G boiled 12 hrs. with 5 g. of KOH in 25 cc. of EtOH, dild. and extd. with Et_2O, yield $CHPh_2OMe$ from MeOH (*Ber.* **36**, 2790(1903); *C. A.* **6**, 1616) and HCO_2H. 27 g. of *p*-anisoin heated 3 hrs. with 94 g. of *p*-BrC_6H_4OMe and 12 g. of Mg in Et_2O, acidified and washed with Et_2O, yield 25 g. of *tri-p-anisylglycol* (I), fine needles from EtOH, m. 176–7°, sol. in C_6H_6 and hot HOAc, sparingly sol. in EtOH, insol. in Et_2O, sol. with intense red-violet color in concd. H_2SO_4. 10 g. of I boiled 1 hr. with 100 cc. 20% H_2SO_4, dild., extd. with Et_2O, washed with dil. NaOH and H_2O and dried with Na_2SO_4, yield 7 g. of *p-trianisylacetaldehyde* (J), needles from MeOH, m. 125–6°, very sol. in Et_2O and C_6H_6, difficultly sol. in cold MeOH, forms an intensely red-violet soln. in concd. H_2SO_4. It does not reduce hot Fehling soln., but reduces boiling NH_3-$AgNO_3$. *Oxime*, silky needles from hot EtOH, m. 166–7°. *Semicarbazone*, prisms from EtOH, m. 175–6°. 3.6 g. of J heated 10 hrs. with 7 g. of KOH in 70 cc. of EtOH, dild., extd. with Et_2O, washed with H_2O, and dried with Na_2SO_4, yield HCO_2H and $(MeOC_6H_4)_3CH$, massed needles from MeOH, m. 45–6°.

C. C. Davis

Isomerization of 1-phenylindene on pyrogenic distillation (a new hydrocarbon). Fritz Mayer and Adolf Sieglitz, with Willy Ludwig. Univ. Frankfurt a. M. *Ber.* **54B**, 1397–402(1921).—The constitution of fluoranthene (A) having been estab-

lished almost with certainty by Meyer and Elbers (*C. A.* **15**, 2277), the authors subjected 1-phenylindene (B) to pyrogenic distn., hoping that, as Ph_2CH_2 yields fluorene, B might give A. The vapor of B was passed over pumice in a porcelain tube heated to dark redness in CO_2 under 16 mm. but instead of A was obtained a ***hydrocarbon***, $C_{11}H_{12}$ (C), isomeric with B, leaflets from alc., m. 167.5°, mol. wt. in boiling C_6H_6 192.8–195. B (13 g.) in 100 cc. of boiling 96% alc. slowly treated with 30 g. Na gives *1-phenylhydrindene*, b_{12} 148–50°. Treated in boiling alc. with the calcd. amt. of aldehyde and a few drops of freshly prepd. alc. NaOEt, B gives the following derivs.: *3-benzal*, yellow needles from dil. alc., m. 77.5°; *3-p-chlorobenzal*, golden yellow needles from alc., m. 95°; *3-p-anisal*, orange leaflets from alc., m. 97°; *1,1'-diphenyl-3,3'-terephthalaldiindene*, $C_6H_4(CH:C.C_6H_4.CPh:CH)_2$, red needles from C_6H_6, m. 231–2°. Boiled 20 hrs. under a reflux with gradual addition of 25 g. $KMnO_4$, 6 g. B yields *o*-$BzC_6H_4CO_2H$. On the other hand, C with aldehydes gives only amorphous products of high m. p., is not reduced by Na and alc. or by H and Pd and is unchanged by $K_2Cr_2O_7$ in AcOH; 0.5 g. boiled 16 hrs. under a reflux with 3 g. $KMnO_4$ yields *o*-$BzCOC_6H_4CO_2H$. *2-Phenylindene*, from 5 g. 2-phenyl-1-indanone allowed to stand 5 days with 5 g. amalgamated Al in moist Et_2O, 1–2 drops H_2O being added every 2–3 hrs., filtered and evapd., the resulting dark oily impure indanol being then boiled 3 hrs. with 5% H_2SO_4, b_{12} 167–70°. *1-Phenyl-2-methylindene*, from 7 g. 2-methyl-1-indanone in 25 cc. Et_2O dropped into 7 g. PhBr and 1.1 g. Mg in 50 cc. Et_2O and boiled several hrs., b_{14} 177°, faintly yellow leaflets from alc., m. 57.5°, is unchanged on pyrogenic distn. 1-Methylindene, b. 99–102°, is likewise unchanged on pyrogenic distn. *1,1'-Dimethyl-3,3'-terephthalaldiindene*, from 3 g. methylindene and 1.5 g. *p*-$C_6H_4(CHO)_2$, orange crystals from C_6H_6, m. 224°. Formulas I and II are suggested as possibly representing the structure of the new hydrocarbon C.



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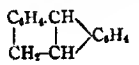
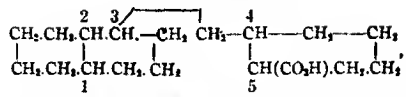


II

CHAS. A. ROUILLER

Naphthalene from a scientific and industrial view-point. E. NOELTING. *Rev. gén. sci.* **32**, 400–5(1921).—A general historical review of the structure and substitution products of naphthalene, with special emphasis upon the derivs. used in the manuf. of colors. T. S. CARSWELL

Hydrogenation of aromatic compounds with the aid of platinum. V. Hydrogenated phenylnaphthylmethanecarboxylic acids. RICHARD WILLSTÄTTER AND ERNST WALDSCHMIDT-LEITZ. Bayer. Akad. Wiss. München. *Ber.* **54B**, 1420–30(1921).—One way of getting around the present scarcity of fatty acids in Germany might be sought in the transformation of easily accessible aromatic substances from coal tar into alicyclic acids. Such substances for the prepn. of alicyclic acids with 14 and 18 C atoms are the keto acids, especially *o*-$BzC_6H_4CO_2H$ and $C_{10}H_7COC_6H_4CO_2H$, obtained from $C_6H_4(CO)_2O$ and aromatic hydrocarbons by the Friedel and Crafts method. These acids can be converted directly with H and Pt into perhydrodiarylmethanecarboxylic acids, the nuclei being hydrogenated first and the ketone groups afterwards reduced. The alk. earth and heavy metal salts of the perhydronaphthylmethanebenzoic acids are characterized by their soly. in hydrocarbons; the alkali salts are soaps, although not as good as those of fatty acids with the same number of C atoms; taking as a measure of the emulsifying power the decrease in surface tension between dil. alkalies and the soln. of the acids in hydrocarbons, they correspond to an aliphatic acid with about 10 C atoms. Of an acid (A) with the structure



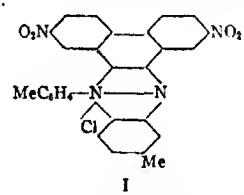
having 5 asym. C atoms (1–5) and possessing no symmetry, 32 isomeric forms are possible but as a part of them can be constructed only by very greatly distorting the mol., the number of isomers is for all practical purposes only 0.5 as large. Thus, for perhydronaphthalene the relations are similar to those for camphor and tropane. For the 2 bridge asym. C atoms common to the 2 rings, only the d_1l_2- and l_1d_2-combinations with converging valences need be considered, as the d_1d_2- and l_1l_2-combinations would require too great a diversion of the valences. In perhydronaphthalene the system is intermol. compensated. A substituent may enter in proximity to either the *d*- or the *l*-bridge atom, so that 2 antipodes are produced; at the same time the entrance of a substituent involves geometrical isomerism with relation to the 2 ring planes; therefore, for a monoalkyl deriv. of the hydrocarbon 4 isomers are possible (2 pairs of antipodes). In A there are in addition the 2 asym. C atoms 4 and 5 in the C_5H_8 ring; according to the geometrical positions of the substituents (H and $CH_2C_{10}H_{11}$) on C atom 4 with respect to the 2 planes of the hydronaphthalene there are produced 2 *cis-trans* isomers which are not mirror images of each other. Each of these 8 possible benzylperhydronaphthalenes, furthermore, on substitution of CO_2H on C atom 5 yields 2 *cis-trans* isomers, according as the H atoms on C atoms 4 and 5 are directed towards the same or towards opposite sides of the cyclohexane plane. These 16 simple isomers combine in pairs to form racemates. Three of these have been obtained pure and a fourth has been erystd. from the sirupy residue but not obtained quite pure. *Perhydrodiphenylacetic acid*, $(C_6H_{11})_2CHCO_2H$, from Ph_2CHCO_2H with Pt without activation, pearly rhombic tablets, m. 137°. The *sodium salt* is easily sol. in excess of soda, the soln. being stable towards $KMnO_4$. The *potassium salt* has a fatty feeling. *Copper*, *ferric* and *silver salts*, light blue, long yellow and colorless needles, resp. The *lead salt* is sol. in C_6H_6. *o*-$PhCH_2C_6H_4CO_2H$ hydrogenated with Pt laden with O yielded *perhydro-o-benzylbenzoic acid* as a non-crystallizable sirup (probably a mixt. of the *cis-trans* isomers), easily sol. in soda, in which it is stable towards $KMnO_4$; the soln. of the K salt hardly foams at all and on standing deposits only a little of the acid salt; the Ca, Ph and Cu salts are easily sol. in Et_2O and C_6H_6. *o*-*α*-$C_{10}H_7COC_6H_4CO_2H$, prepd. by Heller and Schülke's method (*C. A.* **3**, 318), after repeated crystn. from ale. (from which it seps. with 1 mol. solvent) and from AcOEt m. 174° and forms monoclinic sphenoidal crystals, $a:b:c = 1.565:1:1.610$, β 97°54′, (100), (011), (101); 31 g. in 1 l. of hot 25% NH_4OH and 15 g. $CuSO_4$ slowly treated with 200 g. Zn dust, boiled 18 hrs. under a reflux in a slow current of NH_3 and acidified yields 19 g. *α-naphthylmethane-o-benzoic acid* (**B**), elongated, triclinic asymmetric, rhombohedron- and spear-like leaflets from ale. and C_6H_6, m. 146°, easily sol. in cold soda, in which it is quite stable towards $KMnO_4$ although slowly oxidized by it, gives flocculent ppts. with Ca, Ba, Zn, Cu, Fe''' salts; the Pb and Cu salts are easily sol. in Et_2O and C_6H_6. On hydrogenation in warm AcOH **B** after absorbing about 1.5 mols. H deposits an acid (**C**) as a magma of fine leaflets which becomes thicker on further hydrogenation and redissolves only when 5 more mols. of H have been used up. The product (6.3 g. from 8.8 g. B in 47 cc. AcOH) seps. from alc. in long thin prismatic crystals, m. 163°, sol. in 36 parts AcOH at 20° (**B** requires only 18 parts), difficultly sol. in soda at room temp., easily at the temp. of the hand; the Pb and Cu salts are easily sol. in Et_2O and C_6H_6 and sep. from it in needles; 0.1 g. in 20 cc. of 5% Na_2CO_3 decolorizes 1 cc. of 0.1 *N* $KMnO_4$ in 10, 7 cc. in 240 min. (for **A** the values are 1 cc. in 40, 4 cc. in 240 min.); Br in CCl_4 is decolorized immediately. The compn. of **C** corresponds to the *dihydro acid*, although the H is somewhat high (C 81.64–81.74,

H 6.30–6.45). From 1.3 g. C on further hydrogenation in 10 cc. hot AcOH there are obtained, after 1 mol. H has been absorbed, 1 g. unchanged C and 0.2 g. of not quite pure sirupy perhydro acid. The $C_{10}H_7COC_6H_4CO_2H$ also, after absorption of 2 mols. H, yields a *dihydro-α-naphthoyl-o-benzoic acid*, rectangular tables from PhMe, m. 201°, easily sol. in soda, decolorizes $KMnO_4$ only slowly; the Pb salt is sol. in Et_2O and C_6H_6. The *perhydro-α-naphthylmethane-o-benzoic acids* (A) can be obtained only with the aid of Pt which is loaded with O, either from B or, more quickly, directly from the keto acid. The hydrogenation of 6.569 g. B in 30 cc. AcOH with 2 g. Pt at 60–70° requires 3 days, 1 g. Pt transporting about 600 cc. H after each activation; 2.364 g. of the keto acid in 20 cc. AcOH with 1.1 g. Pt was completely reduced in 2 days. The AcOH soln. of the reduction product on standing deposits aggregates of prisms, the first crops crystg. rapidly, the later ones with extraordinary slowness; the final mother liquors on evapn. *in vacuo* leave a very viscous resinous sirup from which no more crystals sep. even after months of standing. In one expt. from 10 g. hydrogenated acid were obtained 3.4 g. m. 96–103°, 2.1 g. m. 92–7° and 1.3 g. m. 88–96°. The first fraction on crystn. from petr. ether yielded 1.5 g. of the *α-form* of A, prisms, m. 129°; the residue (1.7 g.) left on evapg. the petr. ether mother liquor was sepd. by repeated crystn. from AcOEt into the *β-acid*, rhombic tables, m. 114°, and the *γ-acid*, needles, m. 94°. In another expt. in which the product sepd. in numerous fractions the AcOH mother liquor on long standing over soda-lime deposited wart-shaped cryst. aggregates of the *δ-acid* which, after repeated washing with AcOH and pressing between paper, m. 82–4° but on cautious recrystn. was again converted into a viscous sirup. All 4 forms are easily sol. in cold alc., C_6H_6 and CS_2 and show the following resp. solubilities in 20 parts petr. ether, AcOEt and glacial AcOH at 20°: *α*, 2.4, 4.4, quite small; *β*, 10.6, 9.8, quite small; *γ*, 32, 28, 3.3; *δ*, very large, very large, 14.3. The *α*-acid seps. in triclinic asymmetric crystals, $a:b:c$ 0.9641:1:1.0141, α 106°49.5′, β 110°19.5′, γ 83°51′, (100), (010), (001) (101), (0$\bar{1}$1), ($\bar{2}$12), (210), (2$\bar{1}$0). *β*-Acid, triclinic asymmetric, $a:b:c$ 0.6102:1:0.5519, α 101° 24.5′, β 101°52′, γ 90°37′, (100), (010), (001), (110), (0$\bar{1}$1), ($\bar{1}\bar{1}$1). The *γ*-acid also forms triclinic asymmetric crystals but owing to the poor development of the faces no measurements could be made; the same is true of B. The dihydronaphthyl acid also forms triclinic asymmetric crystals, $a:b:c$ 0.7311:1:0.5161, α 108°54′, β 105°44′, γ 93°19′, (100), (010), (001), (101), (212), (012). The perhydro acids are difficultly sol. in cold 7.5% Na_2CO_3; on warming there are formed oily drops of the Na salt which solidify on cooling and dissolve on dilu., addition of soda repptg. them. Aq. solns. of the alkali salts hydrolyze, depositing the acid salt, and foam strongly, although the foam is not so permanent as that of good soaps. The Na salt requires a greater dilu. for hydrolysis than the K salt. The solns. of the alkali salts are ppt. by $CaCl_2$ and heavy metal salts; the metal salts are very sol. in org. solvents. The relative emulsifying power of the soaps was detd. by dissolving 0.1 g. of the acid in 25 cc. of a mixt. of 4 vols. liquid paraffin and 1 vol. PhMe and letting 20 cc. of the soln. flow out of a capillary pipet bent upwards against a column 1–2 cm. high of 0.001 *N* NaOH and counting the drops; below are the ratios [no. of drops hydrocarbon mixt.]: [no. drops acid]: perhydrodiphenylacetic, 0.98; *α*-A, 0.78; *β*-acid, 0.75; *γ*-acid, 0.85; stearic, 0.23. CHAS. A. ROUILLER

The chemistry of acenaphthene and its derivatives. DOROTHY A. HAHN AND HARRIET E. HOLMES. *J. Ind. Eng. Chem.* 13, 822–30(1921).—An outline, accompanied by a fairly complete bibliography. E. J. C.

Dyes derived from phenanthraquinone. EDWIN ROY WATSON AND SIKHIBHUSHAN DUTT. Dacca College, East Bengal. *J. Chem. Soc.* 119, 1211–21(1921); cf. *C. A.* 9, 609; 10, 2583.—Attempts were made to prep. the phenanthraquinone analogs of the anthracene mordant dyes both from the 2,7-$(NO_2)_2$ and the 4,5-$(NO_2)_2$ derivs. but with no success. Attempts to reduce to the NH_2 deriv., followed by diazotization and treat-

ment with NH_4OH, were equally unsuccessful. The oxidation of the 3-NH_2 deriv. likewise gave no interesting product. The attempts to prep. phenanthraquinone vat dyes also failed. *2-Aminophenanthraphenazine*, $NH_2C_{14}H_7(:N)_2:C_6H_4$, from 3 g. 3-$H_2N$-$C_{14}H_8O_2$ and 1.5 g. *o*-$C_6H_4(NH_2)_2$ in 20 cc. alc., yellow prismatic needles from dil. C_5H_5N, m. 220–1°. It dyes wool a bright yellow shade from a 5% AcOH bath. *4-Amino derivative*, dull yellow needles from C_5H_5N, m. above 285°. *2,7-Diamino derivative*, $C_{26}H_{16}N_4$, prepd. in glacial AcOH, brilliant yellow needles from dil. C_5H_5N, dyes light yellow shades on wool. *4,5-Diamino derivative*, similar properties to the 2,7-deriv. *2,7-Diaminodihydrophenanthraphenazine*, $(NH_2)_2C_{14}H_6:(NH)_2:C_6H_4$, from the 2,7-$(NO_2)_2$ deriv. (*Ber.* 36, 3738) by reduction with 15 parts concd. HCl and 2 parts Sn, violet needles from dil. C_5H_5N, does not m. below 280°. The *hydrochloride*, $C_{26}H_{18}N_4.4HCl$, yellow, from which alkali liberates the free base. *Tetraacetate*, $C_{34}H_{32}O_4N_4$, clusters of yellow needles, does not m. below 285°. With $NaNO_2$ the HCl salt gives the *2,7-dihydroxy derivative*, minute brownish yellow needles from $PhNO_2$-AcOH. *2,7,11-Triaminophenanthraphenazine*, $(NH_2)_3C_{14}H_6(:N)_2:C_6H_3NH_2$, by heating 1.2 g. $(H_2N)_2C_{14}H_8O_2$ and 1 g. 1,2,4-$C_6H_3(NH_2)_3$.HCl in 20 cc. H_2O for 0.5 hr., pptg. with AcONa and crystg. from dil. C_5H_5N, yellowish brown, prismatic needles, do not m. below 280°. *Hydrochloride*, violet, which dyes strong yellow shades on wool. *2,7-Diamino-15-hydroxyphenanthranaphthazine-13-sulfonic acid*, $(H_2N)_2C_{14}H_6(:N)_2:C_{16}H_6(OH)SO_3H$, bright yellow flocks, which dye yellow shades on wool. *4,5-Diamino derivative*. *2,7-Dinitro derivative*, fox-red color. *2,7-Dinitro-11,4'-dimethylflavinduline chloride* (I), from 2.9 g. $(O_2N)_2C_{14}H_6O_2$, and 2.2 g. $MeC_6H_4NHC_6H_3MeNH_2$ (*o*) in glacial AcOH, and addition of concd. HCl, golden yellow needles which are easily decompd. The *2,7-diamino derivative*, $C_{21}H_{21}N_4Cl$, may be prepd. by reduction of the di-NO_2 deriv., but owing to its instability it is better to prep. it from 2,7-$(H_2N)_2C_{14}H_6O_2$, dark brown amorphous powder, which decomps. in the steam-oven.



I

Phenanthraquinone-2,7-bis-[2'-azo-7'-amino-1'-hydroxynaphthalene-3'-sulfonic acid], $C_{14}H_6O_2[N_2C_{10}H_4(NH_2)(OH)SO_3H]_2$, by diazotizing 1 g. 2,7-$(H_2N)_2C_{14}H_6O_2$ in 5% H_2SO_4 and pouring the filtered soln. into 2.2 g. 7,1,3-$C_{10}H_5(NH_2)(OH)SO_3H$ in dil. NaOH, allowing to stand 2 days, neutralizing with dil. HCl, concg. to a small vol. and acidifying, dark violet amorphous powder. The *sodium salt* is a typical direct cotton dye but is not a good union dye as it has more affinity for cotton than for wool when dyed from a neutral bath with 10% NaCl. *Phenanthraquinone-4,5-[bis-2'-azo-7'-amino-1'-hydroxynaphthalene-3'-sulfonic acid]*, $C_{44}H_{22}O_{16}N_6S_2$. The *sodium salt* does not give as strong dyeings on cotton as the 2,7-deriv., and the vat is not exhausted. It dyes good reddish violet shades on wool from an acid bath. *Dihydrophenanthraphenazine-2,7-bis-[2'-azonaphthionic acid]*, $C_{30}H_{12}N_2[N_2C_{10}H_5(NH_2)SO_3H]_2$, rhombohedral crystals. It is a direct cotton dye giving reddish violet shades, but the fastness is no better than that of benzopurpurin 4B. *11-Aminophenanthraphenazine-2,7-bis-[2'-azo-7'-amino-1'-hydroxynaphthalene-3'-sulfonic acid]*, $NH_2C_{26}H_8N_2[N_2C_{10}H_4[NH_2](OH)SO_3H]_2$, violet amorphous powder, which is a direct cotton dye but not a good union dye. *2,7-Diaminophenanthraquinonediphenylhydrazine-p,p'-disulfonic acid*, brown, cryst. aggregates;

it is an acid dye giving good warm brown shades on wool but the dyeings are not particularly fast. C. J. WEST

Hydrazones and azines. II. Condensation products of aromatic keto hydrazones with *o*-quinones. OTTO GERHARDT. Hochschule für Bodenkultur. *Monatsh.* **42**, 63–72(1921); cf. *C. A.* **14**, 3409.—*o*-Quinones react with aromatic ketohydrazones to form compds. of the type $R_2C:N_1:R_1:O$. Attempts to cause 2 mols. hydrazone to react with 1 quinone complex, to give a compd. of the type $R_2C:N_1:R:N_2CR_2$, were unsuccessful; this is probably due to steric hindrance. The new compds. were formed by warming mol. proportions of the components in dry C_6H_6 or other hydrocarbons. *Phenanthrenequinobenzophenone ketazine*, $C_{27}H_{18}ON_2$, from 5 g. phenanthrenequinone and 4.72 g. $Ph_2C:NNH_2$ in 50 cc. C_6H_6, deep red crystals from C_6H_6-MeOH, m. 158–9°; yield 52%. *Phenanthrenequinofluorenone ketazine*, $C_{27}H_{16}ON_2$, deep brownish violet crystals, m. 215–6°; yield 45%. *Acenaphthenequinobenzophenone ketazine*, $C_{27}H_{18}ON_2$, pale Cr-yellow, m. 185–6°; 41% yield. *Isatobenzophenone ketazine*, $C_{21}H_{18}ON_2$, canary-yellow needles, m. 214–5°; yield, 60%. *Acenaphthenequinofluorenone ketazine*, $C_{27}H_{14}ON_2$, brownish yellow, m. 193.5–5°; yield 45%. *Isatofluorenone ketazine*, $C_{21}H_{12}ON_2$, light cinnabar-red needles, m. 185–6°; yield 50%. *Thionaphthenequinobenzophenone ketazine*, $C_{21}H_{14}OSN_2$, cinnabar-red crystals, m. 107–8.5°; yield, 30%. *Thionaphthenequinofluorenone ketazine*, $C_{21}H_{12}OSN_2$, dark red needles, m. 221–3°; yield, 25%. *Camphorquinobenzophenone ketazine*, $C_{23}H_{24}ON_2$, by heating the components in a sealed tube at 100° for 6 hrs., colorless powder, m. 106.5–8°; yield 27%. *Camphorquinofluorenone ketazine*, $C_{23}H_{22}ON_2$, nearly colorless powder, m. 156–7°; yield, 25%. C. J. WEST

The production of high-grade anthracene. B. HARDMAN. *Chem. Trade. J.* **69**, 94–5(1921).—Purification of crude anthracene by recrystn. from heavy bases gave anthracene (A) of 80–5% purity. A purer product was obtained by the method of Wirth (Ger. Pat. 122,852; French Pat. 302,998). Crude (38.2%) A was mixed with 1.5 times its wt. of solvent naphtha, and sufficient dil. H_2SO_4 was added to decomp. the $NaNO_2$ to be added; 10% $NaNO_2$ soln. was then run in below 25° with agitation so that no red fumes escaped. The mixt. was filtered and the residue washed with solvent naphtha. By acting for 90 min. upon a mixt. of 100 parts crude A with 10 parts of $NaNO_2$, 96.5% of A having a purity of 83.6% was recovered. A 98.5% yield of a product having a purity of 94.8% was obtained by heating to soln. 380 g. of 81% product purified with $NaNO_2$ with 600 cc. of heavy bases, cooling to 30°, filtering, and washing on the filter with 600 cc. of fresh heavy bases. The recrystd. product was a grayish white cryst. substance, giving by sublimation A of 97% purity. A less pure product was obtained by first recrystg. crude A from heavy bases and then purifying with $NaNO_2$. The residue remaining after recovery of the heavy bases may be reworked, or used as a timber preservative, a source of C black, or a cheap grease. T. S. C.

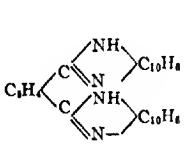
Synthesis of 1,6-dihydroxy-2-methylanthraquinone. JOHN LIONEL SIMONSEN AND MADYAR GOPAL RAU. Forest Research Inst., Dehra Dun. *J. Chem. Soc.* **119**, 1339–48(1921).—*1,6-Dihydroxy-2-methylanthraquinone* (A) was synthesized in an attempt to prove the structure of morindone (*C. A.* **13**, 126), since by the introduction of a 3rd HO group hydroxymethylanthrarufin or hydroxymethylchrysazin would result. While A was synthesized, the 2nd reaction failed. *3-Nitro-2-methoxy-p-toluic acid* (B), $C_9H_9O_5N$, by slowly adding 6 g. 1,2,4-Me(MeO)$C_6H_3CO_2H$ to a well cooled mixt. of 12 g. HNO_3 (d. 1.5) and 24 g. Ac_2O, allowing to stand 15 min., and pouring onto ice, long, prismatic needles from hot H_2O, m. 165–6°. *Amide*, $C_9H_{10}O_4N_2$, long needles from hot H_2O, m. 142°. *3-Nitro-2-methoxy-p-toluidine* (C), by the action of 0.8 g. Br in 35 cc. KOH (1.7 g.) on 1.5 g. of the amide, viscid orange-yellow oil. *Acetate*, $C_{10}H_{12}O_4N_2$, needles from hot H_2O, m. 92–3°. The constitution of C was established by diazotizing with $AmNO_2$ and decompg. with boiling H_2O, when, after hydrolysis of the Me ether,

1,2,3-Me(HO)$C_6H_2NO_2$ was obtained, and also by reduction to the corresponding *diamine*, which was converted by Jones and Robinson's method (*C. A.* **12**, 135) into *phenanthraphenazine*, $C_{26}H_{16}ON_2$, felted, yellow needles from AcOH, m. 187°; the concd. H_2SO_4 soln. was magenta-colored and a neutral soln. exhibited no fluorescence. When 10 g. B in 25 cc. concd. NH_4OH are gradually added to 80 g. $FeSO_4$ in 140 cc. H_2O and vigorously boiled till the reaction has ceased, then concd. until the NH_4 salt begins to sep. and acidified with dil. HCl, *3-amino-2-methoxy-p-toluic acid*, $C_9H_{11}O_3N$, seps., long, prismatic needles from hot H_2O, m. 162°. *Hydrochloride*, rhombic plates. *Sulfate*, minute needles. *Chloroplatinate*, straw-colored needles, decomp. 220°. *Acetate*, long needles from hot H_2O, m. 191°. Diazotized and treated with KCN, *2-methoxy-3-cyano-p-toluic acid* results, $C_{10}H_9O_3N$, slender needles from dil. MeOH. *Silver salt*, short, prismatic needles. Hydrolysis with 75% H_2SO_4 for 3 hrs. gave *3-methoxy-4-methyl-o-phthalic anhydride* (D), $C_{10}H_8O_4$, long needles from C_7H_8, m. 135°. The mother liquor gives the corresponding *acid*, $C_{10}H_{10}O_5$, short prisms, m. 175–6°. *Barium salt*, fine needles. *Imide*, $C_{10}H_9O_3N$, small needles m. 228°. 1 g. D in 10 cc. anisole, treated with 2 g. $AlCl_3$, gave 1.5 g. *4'-hydroxy-2-methoxy-3-methylbenzophenone-6-carboxylic acid*, $C_{16}H_{14}O_5$, balls of radiating needles, m. 218°. *Silver salt*, gaseous white ppt. *Methyl 2,4'-dimethoxy-3-methylbenzophenone-6-carboxylate*, $C_{18}H_{18}O_5$, prismatic needles from MeOH, m. 162°, obtained by the action of MeI and KOH on the acid. In large-scale work the crude acid was not purified but directly transformed into the Me ester. Upon sapon., the *acid*, $C_{17}H_{16}O_5$, was obtained as small needles from dil. AcOH, m. 205–6°. It is easily esterified by Meyer's method. A was obtained by dissolving 1 g. of the acid in 4 cc. H_2SO_4, adding 0.5 g. P_2O_5 and heating 0.5 hr. at 140–50°. The part insol. in KOH is *1,6-dimethoxy-2-methylanthraquinone*, $C_{17}H_{14}O_4$, yellow needles, m. 182°. A was pptd. by acidifying the KOH ext. and purified through the *acetate*, $C_{19}H_{14}O_6$, S-yellow needles, m. 212°, and forms brown, bayonet-shaped needles, m. 281°. The soln. in alkali or H_2SO_4 is red. C. J. West

Nitroamines of the anthraquinone series. Ernst Terres. Univ. Graz. *Monatsh.* **41**, 603–12(1921); cf. Scholl, *Ber.* **37**, 4427, 4686.—*Nitro-1-nitraminoanthraquinone*, $C_6H_4(CO)_2C_6H_2(NO_2)NHNO_2$, is obtained by slowly adding 10 g. $C_{14}H_7O_2NH_2$ to 100 cc. HNO_3 at −10° and stirring for 1.5 hrs., and extg. the nitramine with hot 20% NaOAc, from which the *sodium salt* crysts., yellowish brown; dil. HCl liberates the nitramine as a light brown ppt., which explodes at 149–51° (10–15° lower if slowly heated). If the above reaction is continued for 2 hrs. at −10° and 15 hrs. at 0°, a mixt. of mono- and di-NO_2 derivs. is obtained, which is sepd. by fractional crystn. of the Na salt from 20% AcONa. *2,4-Dinitro derivative*, $C_{14}H_6O_8N_4$, light yellow, decomps. 137–42°, slowly at 100°. The cold concd. H_2SO_4 soln. is reddish brown, the warm soln. red. The soln. in high boiling solvents decomps. 120–30°. *Ammonium aci-salt*, yellow needles. The action of 1 part PhOH in 20 parts concd. H_2SO_4 on 1 part of the nitramine for 4 hrs. gave *2,4-dinitro-1-aminoanthraquinone*, $C_{14}H_7O_6N_3$, light brick-red ppt., m. 270–2°, easily sol. in hot C_5H_5N and $PhNO_2$. This is reduced by $(NH_4)_2S$ to *1,2,4-triaminoanthraquinone*, bluish red powder, which does not m. 300°. With phenanthraquinone it yields *4-amino-1,2-(9',10')-phenanthrazinoanthraquinone*, $C_{28}H_{13}O_2N_3$, brown crystals. *Dinitro-1,5-dinitraminoanthraquinone*, greenish yellow cryst. powder, decomps. 121–2°. *Dinitro-1,5-diaminoanthraquinone*, $C_{14}H_8O_6N_4$, dark red ppt., sol. in dil. NaOH. This was reduced to a *tetraminoanthraquinone*, $C_{14}H_{12}O_2N_4$, blue powder. C. J. West

Condensation of aromatic diamines with phthalic anhydride. II. Hans Lieb and Gustav Schwarzer. Univ. Graz. *Monatsh.* **41**, 573–82(1921); cf. *C. A.* **13**, 1837.—Two parts 1,2-$C_6H_4(NH_2)_2$ and 1 part $C_6H_4(CO)_2O$, intimately mixed and heated in a sealed tube in the presence of burnt lime as a dehydrating agent for 6–9 hrs. at 250–70°, gave *o-phenylenedi-[1,2-naphthimidazole]* (I), yellow rods from alc. or C_5-

H_4N, m. 304°. 0.5 hr. boiling with Ac_2O gave the *acetate*, $C_{32}H_{22}N_4O_2$, rhombic plates, m. 236°. The *benzoate* is formed by treatment with $BzCl$ in C_5H_5N, nearly colorless leaflets, m. 237–8°. When $C_6H_4(CO)_2O$ and 1,2-$C_{14}H_6O_2(NH_2)_2$ are heated in almost any proportions, the product formed is *benzoyleneanthraquinoneimidazole* (II), yellow needles from C_5H_5N, m. 354° (decompn.). Upon warming with NaOH, the lactam ring is broken and the *sodium phenylanthraquinoneimidazole-o-carboxylate* is formed, which was not obtained free from NaOH; it forms dark red needles, hydrolyzed by water. 1,5-$C_{14}H_6O_2(NH_2)_2$ and 2 mols. $C_6H_4(CO)_2O$, when melted in an open vessel, give *1,5-diphthaloyldiaminoanthraquinone*, $C_6H_4(CO)_2NC_6H_3(CO)_2C_6H_3N(CO)_2C_6H_4$, m. 435–6°. With 1 mol. $C_6H_4(CO)_2O$, *monophthaloyl-1,5-diaminoanthraquinone*, $C_6H_4(CO)_2NC_6H_3(CO)_2C_6H_2NH_2$, is formed, m. 331°, which may be sepd. from the less sol. diphthaloyl deriv. by the use of C_5H_5N. The prepn. of *p*- and *m*-phenylenediphthal-



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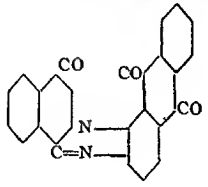


II

imide (*Ann.* 327, 42) may be conveniently carried out by heating 1 mol. *p*- or *m*-$C_6H_4(NH_2)_2$ with 2 mols. $C_6H_4(CO)_2O$ in an open vessel or a sealed tube. *p-Acetylaminophthalanil*, $C_{16}H_{12}N_2O_3$, m. 287–8°. The reduction of the *p*-deriv. with Zn and AcOH gave a variety of products, from which a small quantity of needles, m. 318–9°, was isolated by repeated crystn. from AcOH, which appeared to be a *dihydro derivative*, $C_{32}H_{16}N_2O_4$. The attempted reduction of the *m*-deriv. did not give satisfactory results.

C. J. West

Methyl-1,2-benzanthraquinone series. III. R. Scholl, Christian Seer and Alois Zinke. Univ. Graz. *Monatsh.* 41, 583–602(1921); cf. *C. A.* 7, 1494.—This work had for its primary purpose the synthesis of 3-methyl-4-chloro-1,2-benzanthraquinone. *1-Methyl-2-chloronaphthalene* (A), $C_{11}H_9Cl$, from 26 g. 1,2-$C_{10}H_6MeNH_2$.HCl and 260 g. concd. HCl, which, after diazotizing, was treated with 13 g. CuCl in 130 g. concd. HCl, light yellow oil, b_{12} 144–5°, b_{20} 155°. When treated with about 16 parts HNO_3 (d. 1.5) for 48 hrs. a mixt. of isomeric *nitro-1-methyl-2-chloronaphthalenes* was formed; the less sol. fraction in alc. m. 133–4°, and forms long, fine, light yellow needles. The more sol. fraction, purified from ligroin and then from alc., forms fine yellow needles, m. 70–80°. 1 g. A, 1 g. $C_6H_4(CO)_2O$ and 1 g. $AlCl_3$ in 10 cc. CS_2 heated for 3 hrs., and then for 4 hrs. after the addition of 1 g. $AlCl_3$, forms *1-methyl-2-chloronaphthalene-6-phthaloylic acid* (B), $MeClC_{10}H_5COC_6H_4CO_2H$, small prismatic prisms from C_6H_6, m. 182°. This may be condensed by heating with fuming H_2SO_4 (14% SO_3) for 4 hrs. at 50–52°, or by treating with $SOCl_2$ and heating the chloride in CS_2 with $AlCl_3$, giving *Bz-4-methyl-Bz-3-chloro-1,2-benzanthraquinone*, $C_{19}H_{11}O_2Cl$, yellowish or greenish yellow needles from AcOH or $PhNO_2$, m. 268°. This was also prepd. by diazotizing the corresponding NH_2 deriv. (*C. A.* 7, 1495) and treating with CuCl. By heating with alc. KOH at 175°, *4-methyl-1,2-benzanthraquinone* is formed, light brown needles, m. 216–6°. The concd. H_2SO_4 soln. is a dirty green. The alk. $Na_2S_2O_4$ bath is dark reddish brown, and the dye is oxidized by the air to a light yellow. Upon oxidation with acid $KMnO_4$, anthraquinone-1,2-dicarboxylic acid was formed. The alkali melt of an impure B gave an isomeric *4-methyl-1,2-benzanthraquinone*, yellow-brown needles, m. 225–6°, sol. in

concd. H_2SO_4 with a deep blue color, which, on oxidation with $KMnO_4$ and treatment with Ac_2O, gave an *anhydride*(?), m. 323°, raised to 336–7° on sublimation in CO_2. *4-Methoxynaphthylphenylketone-2-carboxylic acid* (*4-methoxynaphthalene-1-phthaloylic acid*), $HO_2CC_6H_4COC_{10}H_6OMe$, from 10 g. 1-$C_{10}H_7OMe$, 10 g. $C_6H_4(CO)_2O$ and 20 g. $AlCl_3$ in 150 cc. CS_2, and purified through the *sodium salt*, light yellow leaflets, small yellowish needles, m. 192–3°. The *ammonium salt* forms light yellow needles. The soln. in concd. H_2SO_4 is red, which changes through dark brown-red to violet-red on heating. *Calcium salt*, glistening leaflets. The alk. filtrate from the Na salt above contains *4-hydroxynaphthylphenylketone-2-carboxylic acid* (*4-hydroxynaphthalene-1-phthaloylic acid*), $C_{18}H_{12}O_4$, long, fine, yellowish needles from AcOH, with crystal AcOH which is lost at 130°, m. 206–8°. The salts are easily sol. and their solns. are green, while that in concd. H_2SO_4 is red. *1-Naphthylphenylmethane-2-carboxylic acid*, $C_{18}H_{14}O_2$, by reduction of the ketone acid with alkali and Zn dust by boiling for 15 hrs., plates from C_6H_6, m. 145–6°. Preliminary nitration expts. indicated the formation of a mono-NO_2 deriv., but it was not further studied. C. J. West

Dinaphthanthracene series. IV. Bromo derivatives. Ernst Philippi and Fedora Auslaender. Univ. Vienna. *Monatsh.* 42, 1–4(1921); cf. *C. A.* 8, 2364.—6.4 g. $O(CO)_2C_6H_2(CO)_2O$, 30 g. PhBr and 10 g. $AlCl_3$, warmed on the water bath for 2 hrs., gave a mixt. of *p-di-p-bromobenzoylbenzenedicarboxylic acid* (A), $C_{22}H_{12}O_6Br$, which crysts. from 20 parts of boiling AcOH, m. 306–9°. On diln. of the AcOH with H_2O, the *m-derivative* (B) is pptd., m. 256–60°. When 1 g. A is warmed with 30 g. concd. H_2SO_4 for 6 hrs. at 120°, *2,9-dibromo-5,7,12,14-dinaphthanthracenediquinone*, $C_{22}H_8O_4Br_2$, results, greenish yellow or yellowish brown needles, decomp. above 250°. In the same way B gave the *2,10-dibromo derivative*, though the mixt. must be heated to 140–150°. The dye bath and coloring properties of these compds. are very similar to those of dinaphthanthracenediquinone. C. J. West

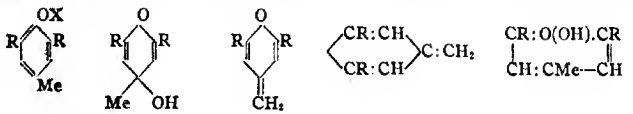
The condensation of water solutions of furfural with aniline. Jack P. Montgomery and E. S. Ernst. Univ. Ala. *Chem. Met. Eng.* 25, 335(1921).—A resin, "furfuraniline," brittle at 25°, and similar to that obtained by Mains and Phillips (*C. A.* 15, 2003), is prepd. by heating aq. solns. of furfural as dil. as 2% with $PhNH_2$ to 125° in an autoclave for 15 min., followed by steam distn. of the excess of $PhNH_2$. The rejected water obtained in the fractionation of furfural may be thus used in the prepn. of furfuraniline. T. S. Carswell

Alkali fusions. III. Fusion of phenylglycine-*o*-carboxylic acid for the production of indigo. Max Phillips. *J. Ind. Eng. Chem.* 13, 759–62(1921).—The phenylglycine-*o*-carboxylic acid (A) used was prepd. by refluxing for about 3 hrs. a mixt. of 137 g. of $C_6H_4(NH_2)CO_2H$, 94.5 g. of CH_2ClCO_2H and 1000 cc. of H_2O. The KOH and NaOH used were 81.2% and 94% pure, resp. After the fusion expts. the cold alk. mass was boiled for 30 min. and then air passed through until all the indigo was pptd.; this was washed with hot dil. HCl, hot H_2O, EtOH and Et_2O, dried at 110° and its purity was detd. Fusion expts. with KOH showed that 260° was the optimum fusion temp., 10 min. the optimum period and 12 to 16 moles of KOH to 1 of A the optimum mixt. With these conditions an 89% yield of indigo of 95% purity was obtained. With NaOH as the condensing agent the optimum conditions (270° temp., 25 to 30 min. fusion period and 28 to 30 moles of NaOH to 1 of A) gave a 69% yield of indigo of about 82% purity. Mixts. of NaOH and KOH gave better yields than NaOH alone, the yield increasing as the amt. of KOH with respect to NaOH was increased. Geo. W. Stratton

Pyranhydrones, a new group of colored, quinhydrone-like addition compounds. Wilhelm Schneider and Heinrich F. W. Meyer. Univ. Jena. *Ber.* 54B, 1484–503(1921).—Phenol ethers reacting with Ac_2O in the presence of $HO_2SCH_2CO_2H$ as catalyzer are substituted in the nucleus while phenols under the same conditions give

only the acetates. When the reaction time is short there is first formed the Me ketone of the phenol ether but if the reaction is allowed to continue longer further changes occur, as shown by the change in color from red-brown to brown- and violet-black. If the solns. are poured into ice water after 24 hrs. and filtered there are obtained generally red solns., in part with green or bluish fluorescence, from which alkalies, alkali carbonates and acetates ppt. amorphous resinous dark violet-blue masses sol. in Et_2O, C_6H_6, $CHCl_3$, etc., with violet-red color; these solns., however, are not stable and change to a dirty dark brown. The original red Ac_2O-$HO_3SCH_2CO_2H$ solns. with $HClO_4$ yield well crystd. red to red-brown perchlorates having the compn. of 4-methyl-2,6-diarylpyrylium salts identical with some of the salts prepd. by Dilthey with Ac_2O and sublimed $FeCl_3$ (*C. A.* **12**, 695). But while D.'s 2,4,6-triarylpyrylium salts give with weak alkalies the colorless pseudo bases, the 4-methyl-2,6-diaryl compds. yield intensely colored blue-violet substances. A study has consequently been made of these blue-violet compds. and in the present paper are given the results obtained with the compds. formed from PhCOMe and PhOMe. According to their compn. they are formed by the loss of 1 mol. H_2O from 2 mols. of the oxonium bases or the pseudo bases (pyranols) corresponding to the pyrylium salts. That they are not compds. of the pyran oxide type is indicated by their intense color, their extraordinary instability in soln. and their ability smoothly to give off another mol. H_2O *in vacuo* at 125°. On soln. in cold AcOH or in concd. H_2SO_4 their color is destroyed and they are decompd. into 2 components of about the same size, one of which can be converted into the pyrylium salt and isolated as the perchlorate while the other forms an amorphous indifferent product which can in no way be transformed into a pyrylium compd. If dil., not too dark solns. of the colored compds. are heated they become markedly lighter but on quickly cooling they reassume their original color intensity. These properties are markedly similar to those of quinhydrones. The hydrolysis of the pyrylium salts (I) (R = aryl) with weak alkalies certainly sets free the oxonium base, which rearranges into the pseudo form (II) and as this, being a tertiary alc., must have a tendency to split off 1 mol. H_2O with the adjacent Me group there is probably formed a compd. (III) which must have residual affinities available at the C atom of the semicyclic CH_2 group and the formation of the blue-violet compds. may be conceived as taking place through the immediate loose combination of each III mol. in the nascent state with another mol. of non-anhydrized oxonium base or II. As quinhydrones are characterized by containing a quinoid component combined with one or more benzoid components and as the III part of the colored compds. has to a certain degree a quinoid grouping preference is given to the true oxonium base structure for the other part of the compd. as representing the benzoid component, and in agreement with Pfeiffer's formulation of the quinhydrones, the colored compds., which are designated "pyranhydrones," are represented by the formula IV. *4-Methyl-2,6-diphenylpyrylium perchlorate* (2.2 g. from 35 cc. Ac_2O heated 15 min. at 80–5° with 5 cc. concd. H_2SO_4, cooled, allowed to stand 1 day with 5 cc. PhCOMe, poured into 250 cc. ice H_2O, filtered and treated with 10 cc. of 20% $HClO_4$), stout yellow table-like crystals from alc., m. 250–60° (decompn.). *Picrate*, brown-red quadratic tables with steel luster from AcOH-H_2O, m. 155°. The $FeCl_3$, C_5H_5N and HNO_3 compds. are identical with Dilthey's. *4-Methyl-2,6-diphenylpyrankydrone* (IV) (4.8 g. from 30 cc. Ac_2O, 5 cc. concd. H_2SO_4 and 10 cc. PhCOMe allowed to stand 24 hrs., poured into 400 g. ice H_2O, filtered after 10 min., freed from PhCOMe and some of the AcOH by 3 extns. with Et_2O and from the Et_2O by 3 hrs. aeration, poured into an equal vol. of cold satd. NaOAc, mixed rapidly, filtered after several hrs., carefully washed on the filter, then 4 times by decantation with 2 l. H_2O and again on a filter and dried *in vacuo*) is a fine amorphous violet-blue powder, begins to shrink about 55°, m. around 90°, mol. wt. in freezing C_6H_6 538.9–545.7, sol. in most of the usual org. solvents

with violet-red color, perfectly stable in the solid dry form in the dark but very sensitive to daylight, unchanged by cold alkalies and by NH_4OH. Although the C_6H_6 or alc. solns. heated a short time near the b. p. become lighter and resume their original color intensity on cooling, in higher boiling solvents (xylene) the color disappears completely if the soln. is sufficiently dil. and is not restored on cooling, and if the alc. or C_6H_6 soln. or concd. xylene soln. is boiled a long time it becomes brown and remains so on cooling. Only from the colored solns. can the pyrylium perchlorate be obtained with $HClO_4$. *In vacuo* at 125° it loses 1 mol. H_2O, leaving a black liquid which solidifies on cooling to a brown-black mass rubbing to a light brown, strongly electrical powder sol. in org. solvents with dark brown color, mol. wt. in freezing C_6H_6 568.8, is strongly unsatd. towards Br, with which it forms an amorphous product. When a fresh Et_2O soln. of **IV** is shaken several times with 20% HCl the violet color quickly changes to brown, the HCl becomes yellow and there seps. a dark resin insol. in either the Et_2O or the HCl, while $HClO_4$ ppts. from the HCl soln. the pyrylium perchlorate; this is also formed immediately when the Et_2O soln. of **IV** is shaken with $HClO_4$ and the resulting brown Et_2O soln. gradually deposits the amorphous brown polymerization product of the "indifferent" part (**B**) of the **IV** mol. If the brown soln. of **IV** in AcOH is treated with much H_2O and then with an electrolyte (*e. g.*, a few cc. of HCl) a gray-green amorphous indifferent substance flocculates out and the AcOH filtrate poured into concd. NaOAc regenerates the **IV**. To follow the course of the cleavage quant., weighed quantities of **IV** were dissolved at room temp. in AcOH of different concns., dild. with several vols. of H_2O after several hrs., treated with a few cc. of HCl, filtered through a weighed Gooch crucible and the pyrylium salt in the filtrate pptd. and weighed as the perchlorate. Assuming that the reaction proceeds according to the equation $C_{36}H_{30}O_3 + HClO_4 = C_{18}H_{11}OClO_4 + C_{18}H_{14}O + H_2O$, there should be obtained 68.3% perchlorate and 48.2% **B**; there were actually found 63.9–66.1 and 43.3–49.4%, resp. Analysis of **B** shows

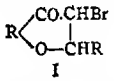


I **II** **III** **IV**

that it takes up H_2O again and really has the same empirical compn. as **IV** and like **IV** loses H_2O on heating *in vacuo;* it is probably a mixt. of hydrated, more or less polymerized transformation products of the anhydro base $C_{18}H_{14}O$; in soly., color of the solns. and behavior on heating (m. around 110°) it greatly resembles the product obtained by dehydrating **IV**. When 10 cc. PhOMe is allowed to stand 0.5 hr. in running H_2O in the Ac_2O-H_2SO_4 mixt., poured into H_2O, taken up in Et_2O, immediately washed with dil. NaOH and dried over $CaCl_2$ there are obtained 5.2 g. unchanged PhOMe and 5 g. *p*-$MeOC_6H_4COMe$, m. 37–8°, b_{760} 265°, $b_{6.0m}$ 108°. If the PhOMe (5 cc.) is allowed to stand 24 hrs. in the Ac_2O-H_2SO_4 and the product, after decompg. with H_2O and filtering, is treated with $HClO_4$ there is obtained 0.6 g. *4-methyl-2,6-di-p-anisylpyrylium perchlorate*, seps. from alc. in brown, from AcOH in orange-red crystals, m. 245° (decompn.); the solns. show an intense yellow-green fluorescence. *Picrate*, finely cryst. brown-red powder from AcOH-H_2O, m. 185°. The $FeCl_3$ salt is identical with Dilthey's. The Ac_2O-H_2SO_4 soln. treated with dil. NaOH gives a gray-green flocculent ppt. sol. in Et_2O with intense violet-red color; Na_2CO_3 produces a similar ppt. but NaOAc only turns the soln. brown and when this is shaken with Et_2O the latter slowly assumes the violet-red color. NH_4OH ppts. dirty-colored flocks (dark blue if the soln. is previously warmed gently and the NH_4OH is added cautiously). *4-Methyl-2,6-di-p-anisylpyran-*

hydrone, from 5 cc. PhOMe allowed to stand 24 hrs. in 40 cc. of Ac_2O-H_2SO_4, decompd. with 400 cc. ice H_2O, quickly filtered, extd. 3 times with Et_2O, aerated, poured into 8 parts cold satd. NaOAc, filtered after some hrs. and washed as described for **IV**, is a fine amorphous dark violet powder, begins to contract 50°, m. around 80°, mol. wt. in freezing C_6H_6 609.9–629.2, loses 1 H_2O *in vacuo* at 125°. *Chloride*, $C_{30}H_{19}O_3Cl.C_{30}H_{20}O_4$, pptd. from the Ac_2O-H_2SO_4 soln. by satg. with NaCl, fine yellow-orange crystals from alc., m. 198°. The pyranhydrone behaves towards acids like **IV**. C. A. R.

Formation of flavones and benzalcoumaranones from hydroxychalcone dibromides. KARL v. AUWERS AND LUDWIG ANSCHÜTZ. Marburg. *Ber.* **54B**, 1543-59(1921).—The bromides of *o*-acetoxychalcones give on treatment with alkali either flavones or benzalcoumaranones, depending on the substituents on one or the other of the C_6H_6 rings. v. Kostanecki and Tambor attempted to explain this difference in behavior by the different ease with which these acetates are hydrolyzed (*Ber.* **32**, 2268(1899)); if the acetate is easily hydrolyzed it first forms the free hydroxychalcone dibromide, which under the further action of the alc. alkali loses the Br in the β-position to the CO group and the H of the HO group as HBr, forming the flavone; on the other hand, if the Ac group is split off only with difficulty, HBr is first split off in the side chain and the resulting α-bromohydroxychalcone gives the benzalcoumaranone. In order to test this view, v. A. and A. have investigated a number of hydroxychalcone dibromides and their acetates and have found that in a number of cases if these compds. are treated in the cold with alc. alkali they yield flavones while on heating benzalcoumaranones are formed. Whether it is possible in all cases to obtain a flavone from the hydroxychalcone dibromide cannot be detd. until more data are available, but the conversion of hydroxychalcone dibromides into benzalcoumaranoes can apparently not be effected in all cases. In the formation of the flavones there is no doubt that there is first formed a compd. of the type **I** which then splits off a second mol. of HBr and forms the flavone; that **I** is not an intermediate product in the formation of the benzalcoumaranone, however, was shown experimentally; probably in these cases the intermediate product is of the type **II**. v. A. and A. believe that in every case both reactions



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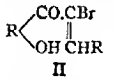


II

go on simultaneously and that the velocity of each is affected differently by the external conditions, in the first place, and, secondarily, by the substituents in both C_6H_6 nuclei. When 200 g. *p*-cresol, 110 g. AcOH and 96 g. $POCl_3$ are gently digested 2 hrs. on the H_2O bath there is obtained 208 g. *p*-MeC_6H_4OAc, b. 209–14°, 100 g. of which, heated 3 hrs. at 120° with 2 parts $AlCl_3$, yields 50 g. 4,2-$MeAcC_6H_3OH$ (**A**). In an attempt to prep. the aldol HOC_6H_3-$MeCOCH_2CH(OH)C_6H_4OMe$, which is probably an intermediate product in the formation of the hydroxychalcone from A and *p*-$MeOC_6H_4CHO$, 5 g. of the A and 4.5 g. of the aldehyde in 50 g. alc. were heated 2 hrs. at 50° with 10 g. of 50% NaOH, allowed to stand until the whole had solidified to a red cryst. mass, suspended in H_2O and treated 1 hr. with CO_2 instead of acidifying with HCl; it was hoped that under these conditions H_2O would not be split off from the aldol but recrystn. of the product from alc. showed that it consisted chiefly of *4-methoxy-2'-hydroxy-5'-methylchalcone* (**B**), with small amts. of *4'-methoxy-6-methylflavanone*, pearly leaflets from MeOH or EtOH, m. 110°; attempts to prep. the latter by boiling **B** with alc. HCl also gave but small yields as the sepn. of the unchanged **B** is difficult. To prep. **B** the red cryst. mass obtained as described above is added to dil. HCl and crystd. from alc.; the **B** seps. in long flat light yellow needles and in stout orange crystals with violet surface luster, m. 98–9°, both forms of crystals belonging to the monoclinic system. *Acetate*, obtained in 80% yield by boiling

10 g. B with 20 g. Ac_2O and 4 g. NaOAc 3–5 min., faintly yellowish needles from MeOH, m. 116°. *Dibromide* (C) (11.3 g. from 10 g. B in the least possible amt. of CS_2 treated with 19.5 cc. Br soln. in CS_2 (1 vol. Br : 9 vols. CS_2)), light yellow granular crystals, m. about 146° (decompn.). *Acetate dibromide* (D) (12.3 g. from 10 g. of the acetate in 300 cc. CS_2 treated with 16.7 cc. Br soln.), elongated crystals, m. 126–7°. If 1 g. C or D suspended in 15 cc. alc. is treated with 6 cc. of 8% NaOH, shaken until the dibromide dissolves, treated with 10 cc. more of NaOH and pptd. with H_2O there is obtained 80% *4'-methoxy-6-methylflavone* (E), fine, felted, silky, faintly yellowish needles from alc. m. 170°, sol. in concd. H_2SO_4 with light yellow color and vivid blue-green fluorescence. On the other hand, if the reaction is carried out in hot soln. the product (20% yield) is *5-methyl-[4'-methoxybenzal]coumaranone* (F), fine canary-yellow needles from MeOH, m. 152°, sol. with blood-red color in concd. H_2SO_4. In an attempt to isolate an intermediate product C was treated with 1 equiv. NaOH as in the prepn. of E and the product recrystd. from Me_2CO-MeOH (1:10), yielding stout crystals turning faintly greenish in a short time, m. 142° not quite clear, solidifies a few degrees higher (apparently with decompn.) and has the compn. (Br, 23.3%) of the expected *3-bromo-6-methyl-4'-methoxyflavanone;* an attempt to prep. the same compd. by cautious bromination of 6-methyl-4'-methoxyflavanone gave a mixt. from which only E could be isolated. Next the C was treated with 1 equiv. NaOH in boiling alc. and after some days large well developed crystals sepd.; repetition of the expt. gave the same product in varying amts. but usually mixed with needles. It was not possible to obtain a const. melting product by recrystn. but the pure substance apprently m. about 107° and is probably *4-methoxy-2'-hydroxy-5'-methyl-α-bromochalcone* (Br, 20.7–21.5%). *4-Methoxy-2'-hydroxychalcone dibromide*, obtained from the chalcone and Br in CS_2 in 68% yield, stout light yellow crystals, m. about 133°; 1 g. of this (or the acetate dibromide) gives by the method used in prepg. E 0.5 g. *4'-methoxyflavone*, m. 157–8°, and [4'-methoxybenzal]coumaranone, m. 126° (Herstein and v. Kostanecki, *Ber.* 32, 318(1899), give 133.5–4.5°), is obtained like F. Similarly 3,4-methylenedioxy-2'-acetoxychalcone dibromide in hot alc. soln. gives [3',4'-methylenedioxybenzal]coumaranone, but in the cold 1.25 g. of the dibromide gives 0.5 g. *3',4'-methylenedioxyflavone*, very fine, faintly yellowish needles from MeOH, m. 200–1°, sol. in concd. H_2SO_4 with light yellow color but no fluorescence, in MeOH with vivid blue-green fluorescence. Attempts to convert 2'-acetoxy- and 2'-hydroxy-5'-methylchalcone dibromides directly into benzalcoumaranones by treating them in hot alc. with excess of NaOH or first into α-bromochalcones and then into the coumaranones always gave either flavones or substances of unknown structure from which no benzalcoumaranone could be obtained. According to Claisen (*C. A.* **14**, 2790), *o*-allylphenol dibromides yield only coumarones, but as he used only the acetates and had to boil them a long time with alc. KOH to transform them into the coumarones v. A. and A. prepd. *o-allyl-p-cresol dibromide*, 4,2-Me($CH_2BrCHBrCH_3$)C_6H_3OH, needles, m. 78.5–9.5° (obtained in 10-g. yield from 20 g. of the cresol in 500 cc. CS_2 and 72 cc. Br soln. in bright daylight), but found that it required 10 hrs. boiling with alc. NaOH to effect complete reaction and that the product was 2,5-dimethylcoumarone, b. 220–1°, $d_4^{11.7}$ 1.0409, n 1.55298, 1.55875, 1.57527, 1.59005 for α, D, β and γ at 11.7°, EΣ 1.01, 1.06, 42%, 47% for α, D, $\beta-\alpha$ and $\gamma-\alpha$, identical with a product prepd. in another way by Claisen.

CHAS. A. ROUILLER

Action of sodium on phenyl acetate. WILLIAM HENRY PERKIN, JR. Dyson Perrins Lab., Oxford. *J. Chem. Soc.* **119**, 1284–94(1921); cf. *J. Chem. Soc.* **37**, 487.—The action of Na on AcOPh gives AcOEt and *o*-$HOC_6H_4CO_2H$, besides 2 substances which P. earlier called α and β. α, m. 68°, has been identified as 2-methylbenzo-α-pyrone, and is found in the fraction b_{18} 130–70°, in addition to dehydracetic acid, and a third *compound*, $C_{11}H_8O_4$, obtained by extg. the oil containing α with K_2CO_3, glistening needles,

m. 137°. $FeCl_3$ in MeOH gives a deep orange color. When evapd. with concd. NH_4OH, a *compound*, $C_{28}H_{17}O_7N$, is formed, needles, m. 237°. The fraction, b_{10} 220–70°, contains β, which was identified as 1-hydroxy-3-methylxanthone, m. 141° (*Am. Chem. J.* 5, 95). *Potassium salt*, $C_{14}H_7O_4K$, yellow. *Methyl ether*, $C_{15}H_{12}O_3$, by repeated treatment of the HO compd. with KOH and Me_2SO_4, prisms, m. 152°, from C_6H_6, glistening needles from AcOEt. Cold concd. H_2SO_4 gives a yellow soln., which is intensified by the addition of HNO_3. The ether is decompd. by MeOH-KOH. *4-Nitro-1-hydroxy-3-methylxanthone*, $C_{14}H_7O_4N$, by warming with dil. HNO_3, and extg. the more sol. 2-isomer with boiling alc., bright yellow laminas from MeCOEt or glacial AcOH, m. 275°. Alc. $FeCl_3$ produces a port-wine color. Cold concd. H_2SO_4 gives an oxonium sulfate (?). The *2-nitro derivative* crysts. from AcMe in voluminous masses of lemon-yellow needles, m. 170°. The alc. soln. gives a deep claret color with $FeCl_3$ and MeOH-KOH ppts, the sparingly sol. K deriv., which crysts. from H_2O in needles. The possible mechanism of these reactions is discussed. C. J. West

Synthesis of γ-alkylated pyridines. Ernst Koenigs and Walter Jaeschke. Univ. Breslau. *Ber.* 54B, 1351–7(1921).—γ-Alkylpyridines can be obtained free from their isomers, although in but moderate yields, by treating 3,1,5-$C_5H_2NCl(CO_2Et)_2$ (A) with sodioalkylmalonates and sapong. and splitting off the four CO_2H groups from the resulting $C_5H_2N[CR(CO_2Et)_2](CO_2Et)_2$ (B). *Diethyl γ-chlorodipicolinate* (A), long needles from PhMe, m. 92–4°, is obtained in 8-g. yield by quickly rubbing 10 g. finely powdered 3,1,5-$C_5H_2N(OH)(CO_2H)_2$ (dried 2 hrs. at 150°) with 34 g. PCl_5, boiling 1 hr. under a reflux provided with a $CaCl_2$ tube, taking up in 50 cc. $CHCl_3$, quickly shaking with 10 cc. ice H_2O, filtering the $CHCl_3$ layer, cautiously treating it with abs. alc. until the violent reaction has slowed down and no more HCl is evolved on further addition of alc., concg. to about 75 cc. and allowing to cryst. at 0°; boiled 0.5 hr. with 20% HCl it yields the free acid. *Tetraethyl dipicolinicmalonate* (B, R = H), fine, long needles from alc., m. 70–2°, is obtained in 1.7-g. yield (1 g. remains in the mother liquors and can be recovered as the free acid by sapon.) by converting 0.8 g. Na into a fine powder by shaking in boiling xylene, pouring off the xylene and replacing it with 100 cc. PhMe, adding 5.5 g. $CH_2(CO_2Et)_2$, heating 2–3 hrs. on the H_2O bath (protected from moisture) until all the Na has disappeared, adding 4 g. A, heating 4 hrs. more on the H_2O bath, pouring off the PhMe, treating the glassy deposit with dil. HCl, taking up the resulting light red-brown oil in Et_2O, drying, cautiously evapg., removing the last traces of Et_2O and PhMe *in vacuo*, rubbing the cryst. magma with 2 parts alc. and letting stand 24 hrs. at 0°; it is sol. in aq. alkalies and when shaken in aq. suspension with $Ba(OH)_2$ instantly gives a ppt. of long, fine needles; 2 g. heated 14 hrs. at 110° in sealed tubes with 20 cc. of 12% HCl gives 0.8 g. of *γ-methylpyridine-α,α'-dicarboxylic acid*, needles with 1 mol. solvent from H_2O, decomps. 245°; 2 g. heated in a distg. flask to 230–40° gives 0.7 g. γ-picoline, b. 141–3°. Similarly, from 6.4 g. $EtCH(CO_2Et)_2$ and 8 g. Na in 100 cc. PhMe boiled 4 hrs. under a reflux with 8 g. A, cooled and shaken with dil. HCl, the PhMe soln. then being evapd. *in vacuo* and the residue boiled 2 hrs. with 10% HCl and repeatedly evapd. with H_2O until the odor of $PrCO_2H$ disappears, is obtained about 4 g. of an acid, apparently a *propylpyridinetetracarboxylic acid*, m. 250–5°, which even after repeated crystns. did not give concordant results on analysis but which on cautious distn. over a free flame gives a moderate yield of *γ-propylpyridine*, b. 184–6°, d_{18} 0.9381, has an intense, C_5H_5N-like odor; *hydrochloride*, long, stout spears from aq. alc., m. 215°; *chloroaurate*, yellow cryst. ppt., m. 113–5°; *chloroplatinate*, brownish yellow ppt., m. 204°; *picrate*, fine silky needles from alc., m. 153°. Chas. A. Roubler

γ-Pyridyl mercaptan and γ-pyridinesulfonic acid. Ernst Koenigs and Georg Kinne. Univ. Breslau. *Ber.* 54B, 1357–62(1921).—*Diethyl γ-mercaptodipicolinate* (0.8 g. from 5 g. of the γ-Cl ester [see preceding abstr.) in 20 cc. alc. and 10.5 g. of 33%

aq. KSH heated 2 hrs. on the H_2O bath), fine, silky needles from alc., m. 176°; in spite of many modifications of the conditions the yield could not be increased. The mother liquors from the above ester, when concd. to a few cc. and treated with alc., yield a gelatinous ppt., apparently of the K salt, which, however, could not be obtained analytically pure and could not be completely decompd. into the free acid even with concd. HCl; it was therefore treated in H_2O with $Pb(NO_3)_2$, yielding the *lead salt*, yellow crystals, 3 g. of which, decompd. in aq. suspension with H_2S, yields 0.7 g. of the free *acid*, fine needles from H_2O, m. 243°, gives a blood-red color with $FeSO_4$, also obtained by boiling the ester with 20% HCl. As distn. of the above acid or its K salt gave only 10–5% of *γ-pyridyl mercaptan* (A), K. and K. turned to γ-C_5H_4NCl, 4 g. of which, heated 6 hrs. in a sealed tube at 140° with an equal wt. of KSH in aq. alc., dild. with H_2O, acidified with AcOH, evapd. to dryness and extd. with alc. yielded 3.8 g. A, yellowish white needles from C_6H_6, m. 177° (decompn.); *chloroaurate*, $(C_5H_4NS.HAuCl_4)_2Au$, brown ppt., m. 210°; *chloroplatinate*, $(2C_5H_4NS\ H_2PtCl_6)_2Pt$, ocher-colored crystals, m. above 335°. *γ-Pyridyl disulfide*, from 0.5 g. A in 4.5 cc. *N* NaOH treated dropwise with 0.6 g. I in KI, long needles from C_6H_6-ligroin, m. 155°; *chloroaurate*, $C_{10}H_8N_2S_2.2HAuCl_4$, greenish yellow crystals, m. 201°; *chloroplatinate*, golden yellow needles, darken about 275°. *γ-Pyridinesulfonic acid* (5 g. from 6 g. A cautiously heated on the H_2O bath with 10 parts HNO_3 (d. 1.2), needles from alc., m. 134–5°; *barium salt*, white needles from H_2O-EtOH; *silver salt*, thick amorphous ppt. C. A. R.

Arylated pyridines and their relations to the corresponding pyrylium compounds. II. Walther Dilthey, *et al.* Univ. Erlangen. *J. prakt. Chem.* **102**, 209–40(1921); cf. *C. A.* **14**, 3084.—Introduction of the Ph nucleus in C_5H_5N (A) has a similar effect to that in NH_3 in that it decreases (1) the soly., particularly in H_2O; (2) the capacity to form salts with acids, and (3) the capacity to add MeI. Introduction of —OMe or —OH in the Ph nucleus increases the basicity, however. Many of the derivs. are fluorescent in HOAc or H_2SO_4, varying from violet-blue to green-blue. No pure green or yellow was observed. A comparison of the properties of arylated pyridines with the corresponding pyrylium compds. proved that (1) the fluorescence of pyrylium compds. is more intense than of the C_5H_5N derivs. and the bases and pseudo-bases do not fluoresce, and (2) the —OMe derivs. of both lose their fluorescence by displacement of the —OMe group. It has been previously asserted (*C. A.* **11**, 449) that the basicity of pyrylium derivs. is increased by the replacement of Me by Ph and the greater the wt. of the Ph nucleus the greater the increase, whereas similar substitutions decrease the basicity of A derivs. This is now modified, for the salt-forming capacity of the pyrylium nucleus is slightly impeded, but the higher Ph derivs. can be prepd., whereas the A derivs. cannot be. Since replacement of N in A by O leads to increase in basicity, it is considered that O is not the primary cause of the basicity of pyrylium compds. Attempts to form the quinopyran deriv. of 2,4,6-triphenylpyridine (B) by a reaction analogous to that for benzopyrylium salts (Decker and von Fellenberg, *C. A.* **2**, 537; **3**, 1004) and for C_5H_5NMeI (*Ber.* **32**, 3116(1899)) were unsuccessful and it was found that whereas the arylated pyrylium compd. showed the characteristics of a Ph_2CH salt, B reacted like A. The pyrylium-$FeCl_3$ derivs. used in some of the syntheses have been previously prepd. (*C. A.* **14**, 199, 2641; **15**, 1291–3). 2,6-Di-*p*-chlorophenyl-4-phenylpyrylium chloride-ferric chloride in EtOH suspension treated with NH_3 until no longer red gives a quant. yield of *2,6-di-p-chlorophenyl-4-phenylpyridine*, fine needles from HOAc or petr. ether, m. 183°, giving a yellow concd. H_2SO_4 soln. and a blue-violet fluorescence in H_2SO_4 and HOAc. *Hydrochloride*, cryst. meal, m. 250°. *Picrate*, small citron-yellow needles from HOAc, m. 236°. *2-β-Naphthyl-4,6-diphenylpyridine*, from the corresponding $FeCl_3$ salt, almost colorless clustered needles from Et_2O, m. 124–5°, insol. in concd. H_2SO_4 (turning yellow), shows a pale green fluorescence in HOAc. *Picrate*, yellow needles from EtOH, m.

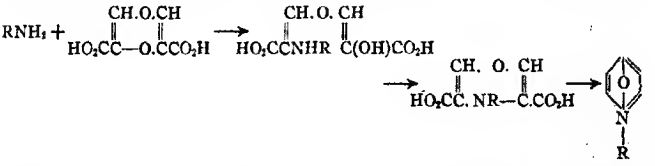
233–4°. *2,6-Di-p-tolyl-4-phenylpyridine*, from the corresponding $FeCl_3$ salt, almost colorless crystals from EtOH, m. 158–9°, insol. in H_2O, difficultly sol. in EtOH, sol. in C_6H_6, giving a violet fluorescence in HOAc or concd. H_2SO_4. *Picrate*, fine, bright yellow needles from HOAc, m. 222°. *Hydrochloride*. *Nitrate*. *2,4-Diphenyl-6-p-tolylpyridine*, almost colorless, brilliant leaflets from EtOH, m. 121°, shows a pale violet fluorescence in HOAc. *Picrate*, bright yellow prisms from HOAc, m. 192°. *Hydrochloride*. *2-Diphenyl-4,6-diphenylpyridine*, long, almost colorless needles from Et_2O, m. 141°, sol. in alc. HCl with yellow color and pale green fluorescence. *Hydrochloride*, intense yellow cryst. meal, decomps. 130° without m. *Picrate*, yellow prisms from EtOH, m. 180°. *2,6-Diphenyl-4-anisylpyridine* (C), brilliant leaflets from EtOH, m. 100–1°, shows a pale yellow color and violet fluorescence in concd. H_2SO_4. *Picrate*, yellow crystals from EtOH, m. 192°. C heated with concd. HCl at 160° for 3 hrs. gives *2,6-diphenyl-4-p-hydroxyphenylpyridine* (D), fine needles from dil. EtOH, m. 214–5°, sol. in EtOH and Et_2O, giving a yellow soln. with pale violet fluorescence in concd. H_2SO_4. It is also prepd. from the corresponding pyrylium-$FeCl_3$ salt. *Picrate*, yellow crystals from EtOH, m. 219–20°. *Iodomethylate* (E), unstable crystals, m. 190° approx., decomp. in the air, gives a yellow-red color in alc. NaOH. *Picrate* of E, yellow needles from EtOH, m. 210°. *2,6-Diphenyl-4-p-acetylhydroxyphenylpyridine*, by boiling D with Ac_2O and NaOAc for 2 hrs., colorless crystals from petr. ether, m. 110–2°, gives no fluorescence in HOAc. *Picrate*, yellow silky needles, m. 170–1°. *2-p-Methoxyphenyl-4,6-diphenylpyridine* (F), wart-shaped crystals from EtOH or gasoline m. 100–2°, sol. in most org. solvents, and in HOAc and concd. H_2SO_4 with bluish green fluorescence. *Picrate*, fine, yellow flakes from EtOH, m. 210°, very sparingly sol. in EtOH. *Methiodide*, unstable crystals. *Hydrochloride*. *Hydrobromide*. *2-p-Hydroxyphenyl-4,6-diphenylpyridine* (G), by heating F with concd. HCl for 2 hrs. at 160°, crystals from NH_4OH containing 0.5 mol. of NH_3, and crystd. from EtOH, m. 189–90°, gives a bluish green fluorescence in acids. *Hydrochloride*, greenish yellow needles from EtOH. *Picrate*, yellow crystals from EtOH, m. 243–4°, very sparingly sol. in EtOH. *Sodium salt*, by boiling G with dil. NaOH, pale yellowish leaflets containing $4H_2O$, m. 100° approx., turning yellow by loss of H_2O. *Potassium salt*, similar to the Na salt. *Acetyl derivative*, by long boiling of G with Ac_2O, needles from Et_2O-MeOH, m. 113–4°. *Methiodide* (H), from heating G with MeI at 120° for 2 hrs., green-yellow, thick crystals from EtOH, m. 208–10°, giving a yellow-red soln. in dil. NaOH (pptd. by HOAc). *Picrate* of H, yellow crystals from EtOH, m. 194°, sparingly sol. in EtOH. *2,4-Di-p-anisyl-6-phenylpyridine* (I), wart-shaped crystals from gasoline, m. 108–10°, giving with HOAc or concd. H_2SO_4 a blue-green fluorescence, changing in the case of H_2SO_4 to blue-violet in 2 hrs. *Picrate*, citron-yellow prisms from EtOH, m. 174–6°. *Hydrobromide*, fine needles from EtOH-Et_2O without definite m. p. *Hydrochloride*. 2 g. of I heated with concd. HCl 4 hrs. at 160–80°, neutralized with NH_4OH and pptd. by H_2O yields 1.8 g. of *2,4-di-p-hydroxyphenyl-6-phenylpyridine* (J), almost colorless or yellow-tinged needles from EtOH, m. 222°, sol. in NaOH without color, in concd. H_2SO_4 with a blue-green fluorescence and in HOAc with a yellow non-fluorescent color. *Picrate*, citron-yellow prisms from EtOH, m. 245°. *Hydrobromide*, yellowish clustered needles. *Hydrochloride*. *Dibenzoyl derivative*, by boiling J with BzCl 2 hrs., colorless needles from EtOH, m. 147–9°. *Methiodide* (K), by heating J and MeI 4 hrs. at 100°, yellow crystals from EtOH, m. 193–4°, giving a yellow-red soln. in alc. KOH. *Picrate* of K, yellow needles, changing in appearance at 134°, m. 198–200°. *Diacetyl derivative* (L), by boiling J with Ac_2O + NaOAc for 2 hrs., pure white crystals from petr. ether, m. 140–1°. *Picrate* of L, small, yellow needles, m. 172°. *2,6-Di-p-methoxyphenyl-4-phenylpyridine* (M), fine, silky, brilliant needles from gasoline, m. 133–4°, sol. in most org. solvents, gives a fluorescence, greenish blue in HOAc, bluish green in concd. H_2SO_4. *Picrate*.

yellow needles from EtOH, m. 193–4°. *Hydrochloride*, green-yellow needles, m. indefinitely 138–55°, sol. in EtOH with intense blue-green fluorescence. *Hydrobromide*, green-yellow needles, m. 160° (not sharply). *Methiodide*, by heating M and MeI at 110–20°, is too unstable to be well purified. M heated with concd. H_2SO_4 4 hrs. at 160–70° gives *2,6-di-p-hydroxyphenyl-4-phenylpyridine* (N), almost colorless, lustrous, silky needles from EtOH, m. 228–9°, sol. in NaOH and HOAc without fluorescence, in concd. H_2SO_4 with yellow color and pale bluish green fluorescence. *Dipotassium salt*, cryst. meal, m. indefinitely, sol. in H_2O and EtOH, turns yellow on heating. *Picrate*, orange crystals from EtOH, m. 256°. *Hydrochloride*, yellow needles, m. indefinitely. *Hydrobromide*, yellow needles, m. indefinitely. *Acetyl derivative* (O), crystals from petr. ether, m. 147–8°. *Picrate* of O, yellow prisms from EtOH, m. 157–9°. *Dibenzoyl derivative*, crystals from EtOH, m. 206–7°. *Methiodide* (P), yellow crystals, m. 228–9° (decompn.), sol. in alc. NaOH with yellow-red color. *Picrate* of P, orange-yellow crystals from EtOH, m. 250–2°. *2,4,6-Tri-p-methoxyphenylpyridine* (Q), fine, white, lustrous silky needles from EtOH, m. 133°, sol. in Me_2CO, Et_2O, C_6H_6, sparingly sol. in EtOH, insol. in H_2O, gives a fluorescence, green-blue in HOAc, bluish green in concd. H_2SO_4. *Picrate*, yellow needles from EtOH, m. 190°. *Hydrochloride*, fine, pale yellow long needles containing more than 1 HCl. By heating to 100° or keeping several weeks *in vacuo*, the excess 1 HCl is liberated, and the residue is deep yellow, m. 150°, insol. in H_2O. *Hydrobromide*, yellow needles, losing HBr at 150°, m. 190° (not sharply). *Methiodide*, cannot be crystd., m. 148° approx., insol. in Et_2O. Q heated with concd. HCl 6 hrs. at 160–70° gives *2,4,6-tri-p-hydroxyphenylpyridine* (R), fine, yellowish white needles from EtOH, m. 282°, sol. in org. solvents and NaOH, insol. in cold H_2O, gives in HOAc and in concd. H_2SO_4 a very pale blue-green fluorescence. *Picrate*, crystals difficult to purify, m. 293° approx., sol. in all org. solvents. *Hydrochloride*, brilliant yellow needles from EtOH, m. 253° (not sharply), sol. in HOAc, EtOH and H_2O (decompn.). *Hydrobromide*, fine, yellow needles, m. 334° (not sharply), sol. in HOAc, EtOH and H_2O (decompn.). *Methiodide*, yellow prisms, m. 228–30°, sol. in alc. NaOH with brown-red color which disappears with HOAc. *Triacetyl derivative* (S), by boiling R with Ac_2O and a little NaOAc for 2 hrs., colorless prisms from petr. ether, m. 158°. *Picrate* of S, brilliant yellow needles from EtOH, m. 182°. C. C. Davis

Pyrocondensations in the pyridine series. Hans Meyer and Alice Hofmann-Meyer. Univ. Prague. *J. prakt. Chem.* 102, 287–94(1921).—A continuation of a study of pyrocondensations (*C. A.* 11, 780; 12, 275, 1296) applied to heterocyclic rings. C_5H_5N (A), α-MeC_5H_4N (B), α,α-$Me_2C_5H_3N$ (C), and α,γ,α-$Me_3C_5H_2N$ (D) were subjected to a bright red heat. The products were fractionated, steam distd., extd. with Et_2O and crystd. They were identified by their picrates and chloroplatinates. From A was obtained α,α-dipyridyl (*Monatsh.* 10, 375(1889)) and as secondary products α,β-dipyridyl (*Monatsh.* 3, 599(1882)) and α,γ-dipyridyl (*Ber.* 19, 360(1886)). From B was obtained *α,α-dipicolyl*, a yellowish oil, with a not unpleasant odor, giving a deep red with excess of $FeSO_4$. Oxidized with $KMnO_4$ it formed no CO_2H acid and partially resinized; *chloroplatinate*, S-yellow fan-shaped crystals, decompg. without melting at a high temp., sol. in hot H_2O with sepn. on cooling of small granular crystals. From C was obtained a *tetramethyldipyridyl*, needles grouped in star shape, m. 55°. The constitution was not established. From D was obtained a *dicollidyl* with 1 H_2O, white odorless mass, m. 66–9°. C. C. Davis

The constitution of *N*-aryl derivatives of 4-γ-pyridone. Alexander P. Smirnoff. Tech. Hochschule. Zürich. *Helvetica Chim. Acta* 4, 599–612(1921).—The formula for arylpyridones is found in the literature as $O{:}C_5H_4NR$, but the reactions do not justify this assumption (*Ber.* 32, 1308(1899)). Five new bases were prepd. in an attempt to explain the constitution. They were all prepd. by condensation of chelidonic acid (A)

with excess of the arylamine at 150–80°. In each case an intense red-yellow appeared at 120°, H_2O was evolved, the mixt. fused, frothed, liberated CO_2 and turned brown. The mass was extd. with warm dil. HCl, filtered, made alk. with NaOH, the unchanged amine removed by steam distn., concd., the base sepd. as an oil, purified if necessary by formation of its HCl salt and liberated by NH_4. The reaction was considered to go in 3 steps.

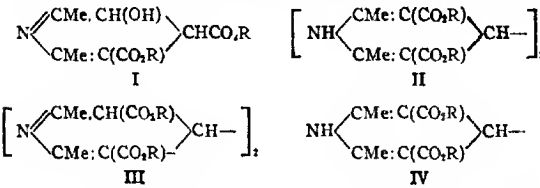


12 g. of A and 28 g. of $PhNH_2$ give 4 g. of 1,4-phenylpyridone (B), flat, white needles from C_6H_6 containing 2 H_2O, m. 125°, sol. in hot H_2O, EtOH, Me_2CO, EtOAc, $CHCl_3$, sparingly sol. in C_6H_6 and its homologs and Et_2O, insol. in petr. ether, dehydrated by $CaCl_2$, gives an intense yellow with $FeCl_3$. It is without action on alkyl halides, acylating compds., NH_2OH, N_2H_3Ph. HNO_2 gives no NO deriv. Hydrochloride, clear truncated plates with 1 H_2O, m. 105° (volatile), dehydrated above its m. p. m. above 330°, sol. in warm H_2O, sparingly sol. in warm EtOH. Chloroaurate, golden needles m. 188°, difficultly sol. in H_2O. Chloroplatinate, fine, orange leaflets, m. 202–8° (decompn.). 10 g. of A and 30 g. of *o*-$MeC_6H_4NH_2$ give 5.2 g. of *1,4-[2-methylphenyl]-pyridone*, rhombic plates from $CHCl_3$ + petr. ether, m. 148°, sol. in Et_2O, C_6H_6 and its homologs and gives a deep yellow color with $FeCl_3$. *Hydrochloride*, thin prisms with 1 H_2O, m. 131° (decompn.). The *gold* and *platinum double salts* are resinous and cannot be crystd. 10 g. of A and 30 g. of *m*-$MeC_6H_4NH_2$ give 4.6 g. of *1,4-[3-methylphenyl]pyridone*, plates from petr. ether + $CHCl_3$, m. 133–4°, very sol. in H_2O, C_6H_6 and its homologs, gives an intense yellow with $FeCl_3$. *Hydrochloride*, thin snow-white needles, m. 92–3°, containing 3 H_2O which is liberated at 120°, giving a glassy mass. *Chloroaurate*, small yellow massed needles, m. 122–3°. *Chloroplatinate*, bright orange-yellow flat needles, m. 205° (decompn.), insol. in org. solvents. 10 g. of A and 30 g. of *p*-$MeC_6H_4NH_2$ give 13 g. of *1,4-[4-methylphenyl]keto-1,4-dihydropyridine-2,6-dicarboxylic acid* (C), massive yellow prisms from H_2O, m. 185° (decompn.), sparingly sol. in hot H_2O, insol. in org. solvents, can be titrated with Me orange. At 185° it decomps. to form *1,4-[4-methylphenyl]pyridone* (D), which is also formed by heating 10 g. of A with 30 g. of *m*-$MeC_6H_4NH_2$ at 175° in 5.5-g. yield or by decompn. of B, massive rhombic spears approx. 4 cm. long, with 2 H_2O, m. 78°, loses H_2O at 120°; the anhydrous compd. m. 142–3°. It is somewhat less sol. than B in the same solvents, and gives an intense yellow with $FeCl_3$. 1 g. of C in 20 cc. H_2O heated at 100° with 5 cc. HOAc and 1 g. N_2H_3Ph, concd., filtered, let stand 1 day, and air-dried gives 1.1 g. of *phenylhydrazone*, brownish plates with greasy luster, of irregular shape, united in rosets, m. 175° (beginning to decomp. 160°). *Hydrochloride* of D, containing 3 H_2O, loses H_2O at 120°, m. 208° (decompn.), difficultly sol. in cold H_2O. *Chloroaurate* of D, fine, golden leaves, m. 178°, sparingly sol. in H_2O. *Chloroplatinate*, small bright orange-yellow crystals, m. 205° (decompn.), insol. in H_2O. 10 g. of A and 30 g. of 2,4-$Me_2C_6H_3NH_2$ give 7.5 g. of *1,4-[2,4-dimethylphenyl]pyridone*, thick colorless prisms from hot H_2O containing 1 H_2O, m. 90°, with soly. similar to D, gives a yellow color with $FeCl_3$. *Hydrochloride*, deliquescent and cannot be crystd. The *gold* and *platinum double salts* are resinous and cannot be crystd. 6 g. of A and 20 g. of α-$C_{10}H_7NH_2$ give *1,4-α-naphthylpyridone* (E), small colorless plates in rosets from hot PhMe, m. 173°, difficultly sol. in H_2O, less sol. in

org. solvents than the preceding derivs. It forms no NO compd., gives an intense yellow with $FeCl_3$. The color reaction of α-$C_{10}H_7NH_2$ is negative. The salts of **E** could not be crystd. C. C. DAVIS

Partial hydrogenation of pyridinecarboxylic esters. OTTO MUMM AND WILHELM BETH. Univ. Kiel. *Ber.* **54B**, 1591–603(1921).—2,6-Dimethylcinchomeronic ester (**A**) (50 g.) in 200 cc. moist Et_2O added to Al activated by Wislicenus' method, heated 2 hrs. on the H_2O bath with 2–3 additions of 1-cc. portions of H_2O, filtered (the pptd. $Al(OH)_3$ being boiled out 1–2 times more with Et_2O), coned. at as low a temp. as possible, made to cryst. by vigorous rubbing and freed from the last of the Et_2O in a vacuum desiccator gives 45 g. *diethyl 2,6-dimethyldihydrocinchomeronate* (**B**), m. 85°, rhombic tables with blue fluorescence from Et_2O, slowly oxidizes in the air but is stable in CO_2; 2.5 g. in AcOH allowed to stand some time with 0.66 g. CrO_3 in 50% AcOH gives 1.7 g. of the original **A**; towards alkalies **B** is very stable at room temp., even a day's shaking, protected from the air, with dil. or coned. alkali producing no change; after several hrs. boiling with NaOH it finally dissolves and on acidification evolves much CO_2; cold NaOEt and hot coned. HCl split off NH_3; alkylation and acylation expts. by the most varied methods failed, but 2.5 g. **B** in 20 cc. dry Et_2O added to 0.2 g. Mg and 1.5 g. MeI in 5 cc. cold Et_2O and warmed a short time on the H_2O bath gave a yellow ppt. containing Mg and I and regenerating **B** with dil. H_2SO_4. In the air **B** changes in the course of several weeks into an oil permeated with crystals; cold dil. HCl dissolves out the oily part and the soln., on being made alk., yields **A** (4.3 g. from 6 g. **B**); the insol. crystals (**C**) (1.5 g.) differ in compn. from **A** by 1 H_2O, m. 156° (gas evolution), can be recrystd. from Et_2O but with great losses as they partially change into **A**; in a desiccator they also gradually become covered with an oily layer of **A**, a change which can be greatly accelerated by heating to the m. p. **C** is probably an intermediate product in the oxidation by air of **B** to **A** and is assumed to have the structure **I**. **B** (10 g.) rubbed with 30 g. soda-lime and distd. over a free flame until the distillate begins to become tarry yields ammoniacal vapors and 2.6 g. 2,6-lutidine. From 5 g. collidinedicarboxylic ester boiled 2 hrs. in 100 cc. alc. with 5 g. activated Al is similarly obtained 3 g. of dihydro ester, m. 130°; in Et_2O or AmOH under the same conditions there is no reaction. In the same way 4-phenyllutidinedicarboxylic ester is reduced to the dihydro ester, m. 156°. On the other hand, 2-methyl-6-phenylcinchomeronic ester cannot be reduced in either alc. or Et_2O with activated Al. When 10 g. granulated Al is etched with 2 *N* NaOH until there is a vigorous evolution of H, washed by decantation with H_2O, treated with 30 g. lutidinedicarboxylic ester (**D**), brought to a boil, treated with 50 cc. of 1% $HgCl_2$, boiled 0.5 hr. longer, filtered hot (the $Al(OH)_3$ being boiled out a few times with 100-cc. portions of alc.), poured into 2 l. H_2O, filtered and dried *in vacuo* over P_2O_5 and KOH there is obtained 28 g. of a (*primary*) *ester* (**E**), $C_{28}H_{36}O_8N_2$, m. about 220° and after resolidifying m. around 70°, seps. as a finely cryst. Cr-yellow powder, best from AmOH, gives no red color in alc. with picric acid, is very sensitive to the acid lab. atm., being oxidized in a few days to **D** with formation of only a very small amt. of the *transformation ester* (**F**) (see below); *in vacuo* over H_2SO_4 it behaves in the same way but yields more **F**; over P_2O_5 the least trace of HCl vapor produces rapid decompn., but over NaOH the **E** is stable for several days. If it is suspended in cold 2 *N* HCl, only small amts. of **D** can be pptd. from the filtrate, even after 12 hrs., by soda but the oxidation proceeds rapidly if the **E** is filtered off and allowed to stand, still moist with the HCl, in the air (thus, in 1 case, 0.6 g. **E** gave 0.26 g. **D** and 0.28 g. **F**). Coned. HNO_3 merely converts **E** into **D** (with much less violence than in the case of the dihydrolutidinedicarboxylic ester (**G**) (condensation ester) obtained by Hantzsch's method (*Ann.* **215**, 1(1882)), as does also HNO_3 acting on **E** in alc. On distn. under 0.5 mm., finally at 260°, 0.35 g. **E** yields 0.16 g. acid-sol. **D** and 0.16 g. acid-insol. **G**. Heated 6 hrs. in CO_2 at 160–70°, 25 g.

E yields 24 g. F, isomeric with E, greenish yellow needles from AmOH, perfectly stable in the air, smoothly oxidized to D by concd. HNO_3, indifferent towards picric acid in alc.; 0.9 g. distd. up to 240° under 0.2 mm. gives 0.3 g. D and 0.58 g. of an acid-insol. product consisting of G contaminated with undecompd. F. M. and B. believe that E has the structure II (cf. Emmert and Buchert, *C. A.* **15**, 2097) and F the structure III. At room temp. E already decomps. to a slight extent into the radical IV, which in the



I II

III IV

air is oxidized to D; at a higher temp. this decompn. is more pronounced and if the air is excluded one part is reduced at the expense of the other, thus giving equal amts. of D and G. CHAS. A. ROUILLER

The Doebner-Miller quinaldine synthesis. WILLIAM HOBSON MILLS, JOHN EDMUND GUY HARRIS AND HERBERT LAMBOURNE. Univ. Cambridge. *J. Chem. Soc.* 119, 1294–1300(1921).—In the synthesis of quinaldine from $PhNH_2$ and AcH, it is generally assumed that the H formed is consumed largely in the production of tetrahydroquinaldine. Large-scale expts. showed, however, that little, if any, tetrahydro deriv. is formed. The following conditions were used. 350 g. AcH in concd. soln. (about 75%) were added to a well stirred mixt. of 300 cc. $PhNH_2$ and 1200 cc. concd. HCl and cooled for 30 min., then 240 g. $ZnCl_2$ added and the mixt. heated for 6 hrs. The secondary bases, sepd. as the NO derivs., consisted of EtNHPh and BuNHPh. *p-Toluenesulfonylethylaniline* (*J. prakt. Chem.* 47, 371(1893)) also exists in a metastable form, m. 68–9° (stable form, m. 87–8°), which yields the stable form when seeded with the same. These sec. bases result from the reduction of the Schiff's bases, MeCH:NPh and MeCH:CHCH:NPh. The tertiary bases consist principally of quinaldine, but contain a small amt. of *6-ethylquinaldine*, b. 276–9°, which was synthesized by the action of 136 g. HCl and 33 g. $ZnCl_2$ upon 45 g. AcH and 49 g. *p*-$H_2NC_6H_4Et$; the constitution was also established by oxidation to 2-methylquinoline-6-carboxylic acid (*Ber.* **23**, 2263). *Dichromate*, m. 134°. *Mercuric chloride salt*, m. 155°. *Zinc chloride salt*, m. 167°. *Methiodide*, $C_{13}H_{16}NI$, yellow needles from alc., m. 214°. C. J. WEST

Kynurenic acid. E. BESTHORN. Akad. Wiss. München. *Ber.* **54B**, 1330–4 (1921); cf. Homer, *C. A.* **8**, 2732.—γ-Methoxyquinaldine (5 g.) and 10 g. com. HCHO heated 48 hrs. on the H_2O bath in a sealed tube, opened, concd. on the H_2O bath to a sirup which no longer smelled strongly of HCHO (this required 8–10 hrs.), taken up in a little cold dil. HNO_3, treated in a large flask with about 90 cc. more HNO_3 (d. 1.4), heated on the H_2O bath until no more red vapors were evolved when the flask was shaken (7–8 hrs.), evapd. on the H_2O bath, digested with cold soda, filtered and concd. yielded a *sodium salt* which, treated in H_2O with AcOH, gave *γ-methoxyquinaldinic acid* (3.8 g.), needles from H_2O, m. 196–7° (evolution of CO_2), gives with $FeSO_4$ in H_2O a faint brown color, deepening on warming, and soon brown-red crystals, probably of an Fe salt, begin to sep. Heated a long time with Ac_2O over a free flame the acid yields a red dye whose dil. C_6H_6 soln. shows a faint fluorescence and soon becomes colorless. From 1 g. of the acid boiled 4–5 hrs. with 8 cc. const. boiling HBr is obtained 0.8 g. kynurenic acid, pptd. from boiling $NaHCO_3$ by HCl in silky flat needles, m. 282–3° (evolution of CO_2); Ba salt, microneedles. The acid, heated a long time with Ac_2O at 140°, soon becomes

blue-red and dissolves in much C_6H_6 with blue color in transmitted light and strong reddish fluorescence in incident light; exposed to sunlight, the C_6H_6 soln. becomes colorless. Heated at 300° until the vigorous foaming ceases, the acid gives kynurene (γ-hydroxyquinoline), m. 201°, identical with Camps' synthetic product. The present work confirms the structure of a γ-hydroxyquinoline-α-carboxylic acid assigned to kynurenic acid by Homer. CHAS. A. ROUILLER

Action of anhydrous hydrazine on nitriles. ERNST MÜLLER AND LEONARD HERRNBERGEN. Univ. Heidelberg. *J. prakt. Chem.* **102**, 113–55(1921).—A study of the action of N_2H_4 (A) on widely different alkyl and aryl nitriles (cf. *J. prakt. Chem.* **50**, 245(1894); **52**, 272(1895)). It was found that by this reaction, dihydrotetrazines were formed in yields which decreased as the homologs of the nitrile advanced to higher members of the series. Dimethyldihydrotetrazine (B) was prepd. according to Curtius, Darapsky and Müller (*C. A.* **10**, 63). Dimethyltetrazine (C) by oxidation of B gave in Et_2O 4 absorption bands, γ 530–40, 542–52, 560–70 and 574–84. C hydrolyzed for the first time by boiling with dil. HCl yields MeCHO, AcOH, N_2H_4 and N. MeC:N.N:CMe.N.N ⟶ MeCH:NN:CMeOH ⟶ MeCH:NNHCOMe ⟶ MeCHO + N_2H_4 + AcOH + N_2. 33.03 g. of EtCN, 19.2 g. of A and 14.1 cc. abs. EtOH boiled 4.5 days liberated NH_3 and yielded diethyldihydrotetrazine (D) and 2.6 g. of diethylaminotriazole, m. 160° (cf. *Ber.* **39**, 1855(1906)). Diethyltetrazine by oxidation of D with HNO_2 gives in Et_2O 2 absorption bands, γ 525–70 and 575–85. Hydrolysis yields N, A and $EtCO_2H$. 3.45 g. of C_4H_7CN, 1.6 g. of A and 2 cc. abs. EtOH boiled 4.5 days give only a trace of the expected dihydrotetrazine. 4.15 g. of C_4H_9CN, 1.6 g. of A, and 1.5 cc. abs. EtOH boiled 4 days liberate NH_3 but give no dihydrotetrazine. 15 g. of PhCN (E) and 4.65 g. of A heated 3.5 days at 100° or 3 g. of E and 0.93 g. of A let stand 6 weeks liberate NH_3 and give dipbenylhydrotetrazine (F). Exposure to the air oxidizes F to diphenyltetrazine (G). In EtOH it gives 2 absorption bands, γ 575–85 and 570–400. Hydrolysis gives PhCHNNHBz with liberation of N (*Ber.* **27**, 1007(1894); *Ann.* **297**, 265(1897)) and traces of BzH and BzOH. 15 g. of $PhCH_2CN$ (H) and 4.1 g. of A boiled 8 hrs. or heated under pressure 3 days at 100° give dibenzyl-*N*-aminotriazole (*Ann.* **298**, 22 (1897)) with liberation of NH_3. No reaction occurs between *o*-MeC_6H_4CN and A. 35.1 g. of *p*-MeC_6H_4CN and 9.6 g. of A boiled 2.5 days give 27.4 g. of di-*p*-tolyldihydrotetrazine (I) with liberation of NH_3. Oxidation of I by HNO_2 or by the air gives di-*p*-tolyltetrazine, with an absorption band in EtOH at γ 518–85. 5.85 g. of *m*-MeC_6H_4CN (J) and 1.6 g. of A heated 5 hrs. at 100–7° give 1.25 g. of di-*m*-tolyldihydrotetrazine (K) with liberation of NH_3. Oxidation of K forms di-*m*-tolyltetrazine. Hydrolysis of K by boiling 0.6183 g. with 8 g. of concd. HCl for 45 min. gives di-*m*-tolylfurodiazole, but 0.4802 g. of K heated with 6.3 g. of concd. HCl 3.5 hrs. under pressure at 120–30° gives *m*-MeC_6H_4COOH (L) and A. The same mixt. of J and A boiled longer than 5 hrs. gives no K, but di-*m*-tolyl-*N*-aminotriazole. Oxidation of 0.5 g. of K gives 0.4 g. of di-*m*-tolyltetrazine (M). This in EtOH has an absorption band γ 520–80. Hydrolysis of M forms N, A and L but no aldehyde. 16.7 g. of β-$C_{10}H_7CN$ and 1.6 g. of A heated several days at 100° give di-β-naphthyldihydrotetrazine (N) with liberation of NH_3. Oxidation of N forms di-β-naphthyltetrazine. Hydrolysis of N with dil. H_2SO_4 yields chiefly di-β-naphthylfurodiazole with smaller amts. of β-$C_{10}H_7CO_2H$. Previous attempts to form the simplest dihydrotetrazine from HCN and A have been unsuccessful (Franzen and Lucking, *C. A.* **5**, 2042). 6.4 g. of A were slowly added with shaking to 5.4 g. of anhydrous HCN (O), the mixt. being kept very cold. Snow-white crystals formed, which upon removal spontaneously decompd. They first melted, sepd. into 2 layers, the upper clear yellow, the lower clear orange. The lower then liberated NH_3, followed by ebullition of the O layer. A white residue proved to be the *compound* N_2H_4CN

(P). The evolution of gas lasted 3–4 hrs. If the liquid reaction product is let stand *in vacuo* and the bright yellow residue thus dried, it yields *dimethinehydrazodihydrazone* ($H_2NN.CHNH-)_2$, (Q). Its formation is attributed to the reaction: $N_2H_4CN \rightarrow HN:CH-NHNH_2$ ($+N_2H_4$, $-NH_3$) $\rightarrow H_2NN:CHNHNH_2$ (2 mols. $-NH_3$) $\rightarrow H_2NN:CHNH-NHCH:NNH_2$. 24 g. of anhydrous HCN in 24 cc. abs. EtOH added to 20 cc. of A in 40 cc. abs. EtOH while cold and kept shaken, the solid product P washed with cold abs. EtOH, gently heated to 55–7° but no higher until evolution of NH_3 ceases, let cryst. *in vacuo*, the white product washed with abs. EtOH and cold Et_2O, let stand over H_2SO_4 until a bright yellow mass results and dried *in vacuo*, give Q, m. 124°. It decomps. spontaneously in the air, forming A and NH_3. Its H_2O soln. reacts strongly alk. 1 g. of Q in 20 cc. H_2O, acidified, shaken with BzH, the ppt. filtered, and washed with Et_2O, yields *dibenzaldimethinehydrazodihydrazone*, $(PhCH:NN:CHNH-)_2$ (R), m. 99° to a clear liquid; yield 2.24 g. per g. of Q. The snow-white product from A and O heated to 120°, the liquid cooled *in vacuo*, dried in the air, dissolved in abs. EtOH and Et_2O added, yields *N*-aminotriazole (*C. A.* 1, 1418). Q acidified with HOAc, HNO_2 added, extd. with Et_2O, the ext. shaken with Zn dust till colorless, neutralized with ZnO, extd. with Et_2O and dried with $CaCl_2$, gives dihydrotetrazine (*C. A.* 1, 1418). Oxidation of this yields tetrazine (*C. A.* 1, 1017), the Et_2O soln. of which has 3 absorption bands, γ 510–20, 530–43 and 553–68. C. C. Davis

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The rare sugars; their purity and tests (Pfansteil, Black) 7. Standardization of the rare sugars (Graber) 7. Theory of valency. II. The configuration of benzene and the organic hydroxyl group (Gnezda) 2. Preparation of petroleum from a vegetable oil (Mailhe) 22. Optical rotary dispersion (Lowry, Austin) 3. Reaction velocity in hydrogenations by platinum black (Vavon) 2. Active racemates (Delépine) 2. The nitration of phenylcarbonates (Horflake) 2. Synthesis of higher order compounds (Pfeiffer) 2. Urotropine (Defrance) 17. Report on the most important articles in the field of pure sugar chemistry published during the first half of 1921 (Lippmann) 28.

Acetaldehyde. H. W. Matheson. U. S. 1,384,842, July 19. See Brit. 132,557 (*C. A.* 14, 288).

Ether from ethylene. C. S. Bradley. U. S. 1,385,040, July 19. Ether is produced by absorbing C_2H_4 in H_2SO_4 at about 140° and introducing superheated steam into the mixt. at a temp. higher than the b. p. of the acid to keep the strength of the acid substantially const.

Perylene. F. Hansgirg. U. S. 1,384,615, July 12. A high yield of perylene is obtained by treating β-derivs. of $C_{10}H_8$ or of α,α-binaphthyl with halogenating agents such as the halogen compds. of P, Sb, As or Al to obtain β-substituted halogen derivs. and then transforming the latter into perylene by the action of ring-closing reagents such as $AlCl_3$ or by the "pyrogene synthesis." A reducing flux such as phosphorous acid is preferably used in the process and it may be carried out as a single operation with isolation of the intermediate halogen derivs. or, if desired, the latter may be separately obtained and used as starting materials for the last stage of the process. Among the starting materials which may be used are: β-hinaphthol; β,β-dichloro-α,α-binaphthyl.

Halogenating toluene or similar hydrocarbons. C. C. Loomis. U. S. 1,384,900, July 19. Halogenation of toluene or its homologs or substitution products, in the side chain, is effected by the action of the halogen, *e. g.*, Cl, in the presence of Na_2CO_3, which serves as a catalyst in the chlorination or bromination of toluene or xylene or their substitution products.

Manufacture of chloro acids. KIKUNAE IKEDA and SHINTARO KODAMA. Japan 37,211, Oct. 4, 1920. By the action of $NaNO_2$, solid or in concd. soln., on amino acid hydrochlorides or their ester hydrochlorides in the presence of HCl, chloro acids or their esters are easily produced. *E. g.*, 1 part leucine or its hydrochloride is dissolved in 1–2 parts of the water layer obtained in the previous manuf. of the chloro acid from leucine and satd. with HCl; the corresponding quantity of 30% $NaNO_2$ soln. is gradually added at room temp. Chlorocapronic acid seps. out as an oil. It is sepd. from the water layer, dried with Na_2SO_4 and distd. *in vacuo*. The method is applied to crude leucine, phenylalanine, valine, alanine, etc.

Treatment of camphor oil. CHŌZŌ SUGIYAMA AND SUZUKI CO. Japan 37,119, Sept. 20, 1920. Terpineol is sepd. as terpinol hydrate from camphor red oil and the residual camphor is extd. from the mother liquor or changed to borneol. *E. g.*, by agitating vigorously a mixt. of 100 parts camphor red oil, freed from safrol by cooling, and 20–30 parts 25–30% H_2SO_4 at 25°, terpinol hydrate seps. as fine crystals; it is collected by filtration and washed with dil. alkali and H_2O. Terpineol is formed from the product by mixing with 100 parts H_2O and 0.5 g. oxalic acid and heating at 110° and then distg. *in vacuo*. Camphor in the mother liquor is isolated by distn. or changed to borneol by the action of Na on the liquor.

Ethyl alcohol from gas containing ethylene. C. A. BASORE. U. S. 1,385,515, July 26. A gas contg. C_2H_4 such as by-product coke-oven gas is caused to react with concd. H_2SO_4 and the resulting mixt. of H_2SO_4 and $EtHSO_4$ is treated with 50–70% its vol. of H_2O and heated in a closed vessel to form alc., which is then distd.

Acetone from sodium acetate. V. DREWSEN. U. S. 1,385,866, July 26. Crystd. NaOAc is melted and heated to about 100°, mixed with about 1/3 its wt. of powdered caustic magnesian lime to dehydrate the material to a whitish powder and then subjected to dry distn. with superheated steam at a temp. of about 300–400° to obtain a yield of acetone equal to about 95% of the amt. theoretically obtainable.

Dehydrating chlorohydrin. W. E. KIRST. U. S. 1,386,118, Aug. 2. H_2O is removed from solns. of glycol chlorohydrin by adding C_6H_6 and heating the mixt. to a temp. at which the combined vapor tensions of the C_6H_6 and H_2O are equal to or greater than atm. or other superimposed pressure, thus effecting the evapn. of C_6H_6 and H_2O while leaving the chlorohydrin behind.

11—BIOLOGICAL CHEMISTRY

HATTIE L. HEFT, EDGAR G. MILLER, JR. AND WILLIAM J. GIES

A—GENERAL

FRANK P. UNDERHILL

Effect of potassium permanganate on the mesenchyme cells of tissue cultures. W. H. LEWIS. *Am. J. Anatomy* **28**, 431–45(1921).—Rapidity of change depends on strength of soln. With 1:40000 or 1:80000 soln. the changes were slow enough to be followed; death occurred in a half-hr. The nucleus showed coagulation changes in a few min., the chromatin contracting and the nuclear sap being expelled in the form of clear vacuoles. Then the mitochondrial threads broke up into rods and granules, becoming more fluid and swollen; the process probably consists of oxidation of phosphatides, since in such oxidation H_2O is taken up. Loss of color reactions indicated cell-death. The centrosphere did not appear to be affected. A. T. CAMERON

Bromine normally present in animal tissues. A. DAMIENS. *Bull. soc. chim. biol.* 3, 95–104(1921).—See *C. A.* 15, 219, 867, 1163. A. T. CAMERON

Experiment demonstrating azotemia. L. HUGOUNENQ AND G. FLORENCE. *Bull. soc. chim. biol.* 3, 174–5(1921).—A small fish is placed in each of 3 vessels, each contg. 3 l. of H_2O, and 2 containing 15 g. urea. Fifty cc. of a 4 % Jack-bean emulsion in 0.4 % acid sodium phosphate are added to one vessel contg. urea and to the third contg. only water. After 0.5–1.0 hr. the fish in the vessel contg. urea and urease becomes agitated, and then succumbs after eclamptiform convulsions. The other 2 remain unaffected. A. T. CAMERON

Nucleic cells. H. MOREL. *Bull. soc. chim. biol.* 3, 176–94(1921).—A review. A. T. C.

Some corollaries of the laws of diastatic hydrolysis. H. COLIN. *Bull. soc. chim. biol.* 3, 263–72(1921); cf. *C. A.* 14, 435, 3253.—The theory previously put forward is applied to develop tests for the purity of certain polyoses, the quantity of enzyme present in a diastatic soln., and the detn. of mol. wts. of a series of sugars which are acted on by a single enzyme, and of which one weight is known. A. T. C.

Chemistry and microscopy of urine for the year 1920. UTZ. *Pharm. Monatshefte* 2, 93–103, 109-18(1921).—A review. Cf. *C. A.* 15, 1545. W. O. E.

Adsorption capacity of commercial charcoals. E. ROSENBERG. *Pharm. Ztg.* 66, 723–4(1921).—After a discussion of the 2 terms, absorption and adsorption, R. describes the examn. of 9 different samples of charcoal (Carbo Sang. Merck, Karbograu, Toxodesmin, Carbo Salicis, Carbo Populi, Carbo Tiliae, Carbo Ligni offic., Carbo Belloc, Carbo Fraudin) *via* Merck-Wiechowski (*in vitro*) and the biol. test of Wiechowski, with the result that the following conclusions appear justified. Blood charcoal possesses a much greater adsorption capacity than wood charcoal, the granulated material being preferable to that of the powdered type provided the granulation causes no diminution of the adsorptive power. W. O. E.

The enzymes of oil-bearing seeds. IX. Oxidases. O. FERNÁNDEZ AND J. LOREDO. *Anales soc. españ. fis. quim.* 18, 43–56(1920).—A general discussion, largely theoretical. A comparison of several methods of detg. catalases in seeds by actual lab. tests on 10 different seeds showed that they do not give concordant results. This is thought to be due to the varying solubilities of the catalases of the different seeds under the conditions of the different tests. L. E. GILSON

Fermentation without yeast. EMIL BAUER AND EUGENE HERZFELD. *Biochem. Z.* 117, 96–112(1921).—Mixts. of substances imitating yeast press juice (*e. g.*, Witte peptone, *d*-glucose, dextrin, $NaHCO_3$, casein, lipoid and bile salts) fermented and produced alc. Toluene, used as an antiseptic, did not ensure sterility. F. S. H.

The physicochemical state of sugar in the blood. K. ONOHARA. *Brit. J. Exptl. Pathol.* 2, 194–6(1921).—As shown by Kozawa, glucose causes swelling of human red corpuscles. But practically the same hematocrit results were obtained with human red corpuscles treated with the serum of a diabetic patient, normal serum with the addition of isotonic glucose soln., or isotonic glucose-saline soln. It may, therefore, be assumed that sugar in the circulating blood is present in the same physicochem. character as in the soln. of free glucose. In other words, it must be present in the circulating blood in the form of free sugar. HARRIET F. HOLMES

A stable single buffer solution, p_H 1 to p_H 12. S. F. ACREE, R. R. MELLON, PAULINE M. AVERY AND E. A. SLAGLE. Rochester, N. Y. *J. Infect. Dis.* 29, 7–10 (1921).—The components of the buffer soln. are: (1) 1 mol. of KH_2PO_4 with a K_a (dissociation const.) of 1.1×10^{-7}; (2) $^1/_3$ mol. of Na formate with a K_a of 2×10^{-4}; (3) $^1/_3$ mol. of Na acetate with a K_a of 2×10^{-5}; (4) the 2nd gronp of K_2HPO_4 with a K_a of 2×10^{-7}; (5) 1 mol. of Na phenolsulfonate with a K_a approx. 10^{-10}; (6) 0.005 *M* thymol

to satn. (for H_3O, 0.08) with an approx. K_a of 0.5×10^{-10}; (7) the 3rd group of H_3PO_4 with a K_a of 10^{-12}. To obtain any desired p_H it is only necessary to locate the point on the curve given in the text that is intercepted by the desired p_H value and read off the amt. of 0.5 *M* HCl or NaOH necessary to produce this p_H. For example, to obtain a p_H of 7.7, add 5 cc. of 0.2 *M* NaOH to 10 cc. of the buffer soln. and dil. to 20 cc. with distd. H_3O. The indicator covering this range is added. JULIAN H. LEWIS

The role of the activity coefficient of the hydrogen ion in the hydrolysis of gelatin. JOHN H. NORTHROP. Rockefeller Inst. *J. Gen. Physiol.* 3, 715–42(1921).—At a const. H-ion concn. the hydrolysis of gelatin follows the course of a monomol. reaction for about $^1/_3$ the reaction. When the H-ion concn. is not kept const., the amt. of hydrolysis at certain acidities is proportional to the sq. root of the time (Schutz's rule). In strongly acid solns. (p_H less than 2.0), the velocity of hydrolysis is directly proportional to the H-ion concn. as detd. by the H electrode, but not proportional to the concn. as detd. by the cond. ratio. "The addition of neutral salts increases the velocity of hydrolysis and the H-ion concn. (as detd. by the H electrode) to approx. the same extent. The velocity in strongly alk. solns. (p_H greater than 10) is directly proportional to the OH-ion concn. Between p_H 2.0 and p_H 10.0, the rate of hydrolysis is approx. const. and very much greater than would be calcd. from the H- and OH-ion concns. This may be roughly accounted for by the assumption that the uncombined gelatin hydrolyzes much more rapidly than the gelatin salt." The methods of exptl. procedure are given at some length. CHAS. H. RICHARDSON

Correlation of the propagation-velocity of the contraction-wave in muscle with the electrical conductivity of the surrounding medium. S. E. POND. Clark Univ. *J. Gen. Physiol.* 3, 807–26(1921).—Muscle tissues from the heart of *Limulus*, the sartorius of the leopard frog and the ventricle of the river terrapin were studied in solns. of graded elec. cond., *i. e.*, mixts. of sea water or Ringer soln. with isotonic sugar soln. "In skeleta muscle, the contraction-wave travels along the fibers at a velocity which is closely proportional to the elec. cond. of the fluid in contact with it. A reduction, by means of diln. with an indifferent non-electrolyte soln., in the elec. cond. of the normal balanced medium is followed by a corresponding reduction in the propagation-velocity of the contraction-wave. This parallelism is closer in solns. of higher than in those of lower elec. cond. The ratio of velocity with respect to cond. is nearly a const. with frog muscle, and less const. with muscles of the turtle and *Limulus*." In the presence of a stream of O, transmission of the contraction-wave is possible in solns. of very low cond., indicating that oxidation processes are directly concerned in stimulation and in the propagation of the excitation state. The role of O is probably to furnish the free O required in the return of the stimulated region to the resting state and in the propagation of the contraction-wave after the local stimulation has been aroused. The local excitation state is probably an effect resulting from the expenditure of energy in the stimulated region accompanying a reduction process; the reverse oxidative process follows automatically when the excited region reaches a max. elec. negativity with respect to adjacent regions. The elec. cond. of the first local stimulating circuit dets. the intensity of the current at any point in the circuit; if the cond. is uniform throughout a tissue and the region surrounding it, the rate of propagation will be uniform throughout the tissue. The sugar solns. used had no toxic action upon the tissues.
CHAS H. RICHARDSON

Donnan equilibrium and the physical properties of proteins. III. Viscosity. JACQUES LOEB. Rockefeller Inst. *J. Gen. Physiol.* 3, 827–41(1921); cf. *C. A.* 15, 1733, 2455.—Gelatin solns. have a high viscosity which in freshly prepd. solns. is influenced by the H-ion concn. similarly to that of the swelling, osmotic pressure, and e. m. f. Under the same conditions, solns. of cryst. egg albumin have a com-

paratively low viscosity which is practically independent of the p_H above 1.0. This difference in the viscosities of the two proteins appears to be related to the tendency of gelatin solns. to form jellies while the egg albumin solns. form no jellies at a low temp. and p_H above 1.0. According to accepted formulas for viscosity, the difference in the order of magnitude of the viscosity of the 2 proteins should correspond to the difference in the relative vol. occupied by equal masses of the 2 proteins in the same vol. of soln. Though it is generally assumed that these differences are due to the hydration of the isolated protein ions, expts. on the effect of p_H on the viscosity of gelatin, amino acids, and cryst. egg albumin showed that this is not true. Five % solns. of glycocoll and alanine and 3% solns. of egg albumin showed no change of viscosity at p_H greater than 1.0, while gelatin had a minimum viscosity at 4.7 (its isoelec. point) and a max. viscosity at 2.7, which dropped again with a further increase in H-ion concn. Suspensions of powdered gelatin in water had a slightly higher viscosity than gelatin solns. of the same concn.; these suspensions were influenced similarly in regard to viscosity by the p_H as were freshly prepd. gelatin solns. The vol. occupied by the gelatin in these suspensions varies similarly as the viscosity, agreeing with the theories of viscosity. The influence of p_H on the vol. occupied by the gelatin granules in suspension is due to the existence of a Donnan equil. between the granules and the surrounding soln. CHAS. H. RICHARDSON

Adsorption of moisture by gelatin in a saturated atmosphere (SHULL, SHULL) 2.

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

Preparation of colloidal gold solution for testing spinal fluid. A. O. GETTLER AND J. W. JACKSON. New York. *Arch. Neurol. Psychiatry* 6, 70–1(1921).—In a clean 1.5-l. Florence flask place 1 l. H_2O (distd. in Cu vessels from $KMnO_4$), and add in turn 10 cc. 1 % $AuCl_3$ soln., 7 cc. 2 % K_2CO_3, and 0.5 cc. 1 % $H_2C_2O_4$, heat to boiling, and then remove from the flame and shake vigorously; while the liquid is still in motion add 0.2 to 0.3 cc. concd. HCHO and shake for 1 min. After 3 or 4 min. the color usually commences to develop. If it does not, again shake, and add an additional 0.1 to 0.2 cc. HCHO, and keep shaking. The color should develop rapidly to deep red.

A. T. CAMERON

Nitrogen titratable by Kjeldahl's method. W. MESTREZAT AND MARTHE P. JANET. *Bull. soc. chim. biol.* 3, 105–30(1921).—A review of the variations employed in Kjeldahl's method and of the results obtained, leading to the conclusion that in all cases these can only be regarded as minima. A. T. CAMERON

Fats and lipoids of blood. P. LEMELAND. *Bull. soc. chim. biol.* 3, 134–69(1921).—L. has studied carefully the methods of Kumagawa-Suto (cf. Adberhalden's Handb. f. Arbeitsmethoden, 4, 483(1911)) for total unsaponifiable content, and of Windaus (cholesterol), the combination proposed by Mayer and Schaeffer (*C. A.* 6, 1447), and Grigaut's method (*C. A.* 8, 147). The results from these methods cannot be compared; they relate to various combinations of fatty acids and cholesterol. A comparison of the detn. of lipoid-P by Neumann's method, as modified by Kleinmann (*C. A.* 14, 2357) and by Grégersen (*C. A.* 2, 1251), that of Raper (*C. A.* 9, 813), and that of Posternak (*C. A.* 14, 2898, 3382), shows that the latter is more reliable. The following technic is recommended: Ppt. 30 cc. of serum by alc., filter, and ext. by the Kumagawa procedure, evap. the alc. of pptn. and extn. to dryness, and ext. the dry residue 3 times with anhydrous Et_2O. Use the residue insol. in Et_2O to measure soaps by sapon. in an autoclave at 120° for $^1/_2$ hr. with 50 % NaOH, applying to the sapon. liquid Kumagawa's method, which gives the wt. of fatty acids corresponding to soaps. Evap. the Et_2O ext. and redissolve in 30 cc. alc. Det. free cholesterol in 5 cc. with

digitonin. Det. lipoid-P in 5 cc. by Posternak's method. Saponify the remaining 20 cc. by the Kumagawa-Suto method and use to det. (*a*) the total ext., less the fatty acids of the soaps (portion sol. in petroleum ether), (*b*) the total fatty acids (less those of the soaps) by treatment of the petroleum-ether soln. with alc. KOH, the part insol. in alc. KOH constituting (*c*) the total unsaponifiable substances, and in this portion cholesterol is measured with digitonin, and the residue consists of "unsaponifiable X." This "unsaponifiable X" has hitherto been included either with cholesterol, or with the total fatty acids, according to the procedure used. The fraction is composed of compds. volatile at a relatively low temp. (below 100°). They amt. to 30–50% of the cholesterol present. Full details of the procedures compared are included.

A. T. CAMERON

Elementary microchemical analysis of organic iron. M. NICLOUX AND G. WELTER. Strasbourg. *Bull. soc. chim. biol.* 3, 170–2(1921).—By Pregl's technic, with a Kuhlmann microbalance, Fe is estd. in small quantities of such compds. as hemoglobin and hemin by calcination with HNO_3 in a Pt crucible, weighing as Fe_2O_3, reduction with H to det. weight of O by difference, from which Fe is calcd. The procedure occupies 15 min., and allows an accuracy within one %. It cannot yet be applied to mixts. such as blood.

A. T. CAMERON

Manganimetric microdetermination of glucose. Application to blood and to cerebrospinal fluid. G. FONTÈS AND L. THIVOLLE. Strasbourg. *Bull. soc. chim. biol.* 3, 226–37(1921).—A further modification of Derrien and Fontès' modification (*Bull. soc. chim.* 27, 327) of Folin and Wu's procedure (*C. A.* 14, 2353). The following reagents are employed: (1) An alk. Cu tartrate soln., prepd. in 2 parts, (*A*) $CuSO_4 \cdot 5H_2O$ 17.5 g., H_2SO_4 2.5 cc., with H_2O to 1 l. (*B*) Add about 200 cc. H_2O to 80 g. anhydrous Na_2CO_3, then 15 g. tartaric acid, and after soln. make up to 1 l. with H_2O. To use, mix in equal proportions, and boil for 1 min. (the reagent is sensitized). There is a negligible reduction. After mixing, the reagent can be used for 24 hrs. (2) and (3) satd. solns. of $MgSO_4$ and Na_2CO_3 kept in dropping bottles. (4) A phosphomolybdic soln. prepd. by mixing 40 g. NH_4 molybdate, 60 cc. NaOH aq. (d. 1.36), and 100 cc. H_2O, and boiling until evolution of NH_3 ceases. Cool. Add 200 cc. H_2O and 200 cc. H_3PO_4 (d. 1.38). Boil for 15 min. Cool. Add H_2O to 1 l. (5) 0.08 % $KMnO_4$. (6) 0.1 % pure anhydrous glucose, preserved under toluene. (7) 10% $Na_2WO_4 \cdot H_2O$. (8) $^1/_3$ *N* H_2SO_4. Method for amts. of glucose between 0.1 and 1 mg.: To 3 centrifuge tubes add measured quantities of sugar soln. to be estd.; to a fourth, 1 cc. 0.1 % glucose soln. Add water to 2 cc., then 1 cc. of soln. (1). Mix, immerse the tubes for 6 min. in boiling H_2O, remove, and without cooling, to each add 5 drops satd. $MgSO_4$, and 4 drops satd. Na_2CO_3. This operation must be completed within $^1/_3$ min. Place the tubes again in boiling H_2O for 1 min., almost fill with boiling H_2O from a fine jet, and centrifuge, decant and at once add 5 cc. of soln. (4). Shake, and wait at least 5 min. for max. appearance of the blue color. Then to each tube add drop by drop from a buret the $KMnO_4$ soln. until the color completely disappears (without reaching a persistent rose tint). The ratio between the number of cc. required for the unknowns and the control gives the amt. of glucose. For amts. of glucose between 0.01 and 0.1 mg. a standard 0.01 % glucose soln. is used, vol. in each tube is made up to 1 cc., 0.5 cc. of soln. (1) and 2 cc. of soln. (4) are used and the microburet is employed for the titration. For *blood*, pipet 1 cc. accurately to a small vial with rinsing and dilu. to 8 cc., add 1 cc. Na_2WO_4 and 1 cc. H_2SO_4. Shake, and after the protein ppt. has settled, filter through a folded paper. Compare 2 cc. with 1 cc. of the standard soln. For measurement with *cerebrospinal fluid* (1 cc.) half the amts. of tungstate and acid are used. The procedure can be suspended without error either after defibrination or after the production of the max. blue color with phosphomolybdate. The following ad-

vantages are claimed for the method: there is no colorimetric comparison; tables are not necessary; the manipulation is short and easy, 3 analyses requiring ¾ hr.; the error usually observed is 3–5 % for amts. of the order of 0.1 mg. and 8 to 10 % for amts. of lesser order. A. T. CAMERON

Determination of sugar in urine. J. C. VAN DER HARST AND C. H. KOERS. *Pharm. Weekblad* 58, 1230–2(1921).—The recent method of Causse and Bonnaus was compared with the fermentation methods of Wagner and of Stephan and with the polariscopic method, and found to be unreliable. A. W. DOX

Method for the colorimetric estimation of carnosine. W. M. CLIFFORD. *Biochem. J.* 15, 400–6(1921).—A modification of Koessler and Hanke's method for estg. imidazole derivs. (*C. A.* 13, 3200) which depends upon the red color obtained when imidazole compds. are treated with diazobenzenesulfanilic acid ("diazo reagent") and Na carbonate. *Method.*—A weighed amt. of finely minced tissue is extd. for 15–60 min. in a known vol. of water. This is then filtered through a dry paper into a dry beaker and the pulp well squeezed out. 2–20 cc. of 20% HPO_3 acid, depending upon the amt. of tissue taken, are added and the mix. is left to stand 2–24 hrs. The soln. is then filtered from the pptd. protein. An aliquot part of the filtrate is placed in a graduating flask, neutralized to litmus with 10% NaOH and made up to the mark with distd. water. This neutralized soln. is treated as a carnosine soln. 10 cc. of 1.1 % Na carbonate are placed in a dry beaker with 2 cc. distd. water, 4 cc. of the "diazo reagent" are run in, and the whole is mixed by shaking the beaker. One min. later 2 cc. of the ext. are added. The standard is a mixt. of methyl orange and Congo red, as described by Koessler and Hanke. BENJAMIN HARROW

Method for the preparation and recrystallization of oxyhemoglobin. H. W. DUDLEY AND C. L. EVANS. London. *Biochem. J.* 15, 487–88(1921).—The method depends on the facts that corpuscles are laked by water and that oxyhemoglobin is less sol. in water than hemoglobin. Defibrinated horse blood is centrifuged and the corpuscles are washed by aid of the centrifuge with isotonic saline soln. until the supernatant liquid gives no turbidity when heated to boiling. The thick corpuscle paste is transferred to collodion tubes and dialyzed under the pressure of a column of mercury, first against running tap water for about 3 days, and then against frequent changes of distd. water for about 2 days. The corpuscles are completely laked and the hemoglobin becomes partly reduced during this operation, a deep purple soln. being obtained. This is centrifuged and can be poured off from the deposit of stromata, etc. O is next bubbled through the clear soln. until crystn. of the oxyhemoglobin occurs, usually about 20 min. The pasty mass is centrifuged, and the oxyhemoglobin settles to the bottom as a thick scarlet paste. This ppt., unlike that obtained when reagents that tend to denature proteins are used, is completely sol. in water. BENJAMIN HARROW

An improved method of determining urea in urine by means of urease. ANDREW M. ROMAN. Chicago. *J. Urol.* 4, 531–40(1921).—A modification of Folin's Nesslerization process is described. JULIAN H. LEWIS

A method for the determination of blood volumes. ELIZABETH FRANKE AND STANLEY R. BENEDICT. Cornell Univ. Med. College, N. Y. *J. Lab. Clin. Med.* 6, 618–24(1921).—The simplest methods of blood-vol. detn. depend on the introduction into the circulation of a non-diffusing, non-toxic, highly colored substance, the concn. of which can be estd. colorimetrically in the plasma. Hemoglobin fulfils these requirements. In the authors' method a preliminary sample of blood is withdrawn, from which the plasma vol. is detd. by sedimentation of the corpuscles. A hemoglobin standard is prepd. with the plasma thus obtained, by the introduction of a soln. of laked red blood corpuscles. A known amt. of the same hemoglobin prepn., corresponding to a given amt. of the standard, is then injected intravenously. A few min. later a sample of blood

is withdrawn and the hemoglobin concn. in the plasma compared with the standard. From the concn. and the plasma percentage the total blood vol. can be calcd. It is about $^1/_{11}$ of the wt. of a normal dog. E. R. LONG

A clinical method for the quantitative determination of calcium and magnesium in small amounts of serum or plasma. BENJAMIN KRAMER AND FREDERICK F. TISDALL. Johns Hopkins Univ. *Bull. Johns Hopkins Hosp.* 32, 44–8(1921).—The method is a modification of the technic of McCrudden (*C. A.* 4, 1493) and permits quant. pptn. without removal of the proteins or ashing of the sample. The max. error is ± 5% and the Ca detn. may be completed within 2 hrs. after the sample is obtained. For the most satisfactory results the detn. should be done within 24 hrs. The blood may be obtained by venipuncture or the Blackfan method. The clotted blood is centrifuged and the serum poured or pipetted off. If Na citrate is used to prevent clotting, its final concn. should not exceed 1.5%. Samples showing moderate or marked hemolysis cannot be used unless treated as follows: Dil. 2 cc. of serum with 2 cc. of H_2O and add 1 cc. of 30% $AcONH_4$. After 1 hr. make up to 6 cc., centrifuge for 15 min. and siphon off the supernatant fluid. Use 5 cc. of this and proceed as for non-hemolyzed serum or plasma, making the proper correction as only $^4/_6$ of the original 2 cc. of serum is used in the analysis. *Detn. of Ca.* Measure 1 or 2 cc. of serum or plasma into an ordinary 15-cc. graduated centrifuge tube containing 2–3 cc. of distd. H_2O, shaking gently after the addition of each drop of serum. Add 2 drops of 0.01% phenolsulfonethalein and 1 drop of approx. 0.1 *N* H_2SO_4. Add 1 drop of 30% NH_4Cl and then 1 cc. of approx. 0.1 *N* $H_2C_2O_4$, shaking after each addition. Add 0.5 cc. of a satd. soln. of AcONa and allow the tube to stand for at least $^1/_2$ hr. The p_H at this point is about 5.4, an acidity which prevents contamination of the ppt. with phosphates. Make up to definite vol., preferably 6 cc., and centrifuge for at least 20 min. at 1,300 r. p. m. Siphon off all but 0.2–0.3 cc. of the supernatant fluid (save for the detn. of Mg if desired) through a glass tube, the lower end of which is drawn out to a bore of about 1 mm. and curved so that the opening is directed upward. The opening of the tube should be at least 3–4 mm. above the ppt. Suspend the ppt. in the residual liquid by stirring with a glass rod. Add enough 2% NH_4OH (2 cc. of concd. NH_4OH dild. to 100 cc.) to bring the vol. to 4 cc., washing the rod and sides of the centrifuge tube free from adherent $H_2C_2O_4$. Centrifuge for 10 min. Repeat this procedure twice, making 3 washings in all. After the 3rd washing, siphon off the supernatant fluid, shake the tube to suspend the ppt., then add 2 cc. of approx. 0.1 *N* H_2SO_4. Warm the tube in a boiling water bath for a few min. and titrate with 0.01 *N* $KMnO_4$ until a definite pink color persists for at least 1 min. when viewed under a good light against a white background. Det. the strength of the $KMnO_4$ soln. by titrating against 0.01 *N* $Na_2C_2O_4$ (dissolve exactly 6.7 g. of $Na_2C_2O_4$ in H_2O, facilitating the soln. by adding 5 cc. of concd. H_2SO_4, then make up to 1 l.; dil. 10 times to make a 0.01 *N* soln. which will remain unchanged for 2 months. The *N* soln. keeps indefinitely.) Cc. of $KMnO_4$ used —0.02 cc. (blank) × 0.02 = mg. of Ca in sample used; express results in mg. per 100 cc. of serum. *Detn. of Mg.* Measure 5 cc. of the supernatant fluid from the Ca detn., corresponding to 1.66 cc. of serum, into a 30-cc. beaker and add 1 cc. of $(NH_4)_2HPO_4$ soln. (dissolve 25 g. of $(NH_4)_2HPO_4$ in 250 cc. of H_2O, add 25 cc. of concd. NH_4OH and allow to stand overnight; filter, boil to remove excess of NH_3, cool and make up to 250 cc. Dil. this soln. 5 times with H_2O). Add 2 cc. of concd. NH_4OH and allow to stand overnight. Filter through a well packed Gooch crucible and wash 10 times with 5 cc. of a mixt. of 10 parts of concd. NH_4OH and 90 parts of H_2O, then twice with 95% alc. made alk. with NH_4OH. Return the crucible to the beaker and dry for a few min. at 80° in an oven. Add 10 cc. of 0.01 *N* HCl to the crucible and after a few hrs. transfer the whole of the material to a test-tube, centrifuge and measure 5 cc. of the supernatant fluid into a flat-bottomed color-

imeter tube graduated for 10 cc., containing 2 cc. of $Fe(SCN)_3$ soln. (prepd. from two solns. which are mixed 1 hr. before use; soln. *A* is 0.3% NH_4SCN; soln. *B* is 0.3% $FeCl_3$ made up from the crystd. salt with the addition of a few drops of HCl if necessary to clear the soln.; mix 5 cc. each of *A* and *B* and dil. to 40 cc. with H_2O). Make up to 10 cc. with 0.01 *N* HCl, insert a rubber stopper and mix. Prep. a series of standards by adding varying amts. of a known $MgNH_4PO_4$ soln. to 2 cc. of the $Fe(SCN)_3$ soln. and make up to 10 cc. as in the unknown samples. (Dissolve 0.102 g. of air-dried $MgNH_4PO_4.6H_2O$ in 100 cc. of 0.1 *N* HCl and dil. to 1 l. with H_2O; 1 cc. = 0.01 mg. of Mg.) Com. prepns. of the salt are unreliable; it should be prepd. by pptn. of pure solns. Compare the color by looking through the entire length of the liquid column against a white background. Reading (cc. of standard soln.) × .01 × 2 × $^{10}/_{1}$ × 50 = mg. Mg. in 100 cc. of serum when 2 cc. of serum are used. Also in *J. Biol. Chem.* **47**, 475–81 (1921); cf. *C. A.* **15**, 2461. A. P. Lothrop

Methods for the direct quantitative determination of sodium, potassium, calcium and magnesium in urine and stools. Frederick F. Tisdall and Benjamin Kramer. Johns Hopkins Univ. *J. Biol. Chem.* **48**, 1–12(1921).—The methods described are rapid and only 50 cc. of urine or 2 g. of dry stool are required for the analysis. The error in the detn. of K is within 1 or 2% and within 3% in the detn. of Ca and Mg. *Prepn. of material. Stools.*—Collect the stool for a measured period in a weighed porcelain dish and heat it on a water bath until dry. Add 95% alc. and evap. Repeat this procedure once. Dry thoroughly over a water bath. Weigh the dish and contents, thus detg. the wt. of the air-dried stool. Grind the dry material to a fine powder and place in a stoppered container. Weigh out 2 g. of the material in a Pt crucible. Place the crucible in a quartz dish 10 cm. in diam. and 6 cm. deep, in the bottom of which are several pieces of porcelain. Gradually heat the outer dish with a Meker burner until no more fumes are given off when the flame is turned on full. Cover the dish with a quartz plate and continue to heat for 1.5 hrs. Wash an ash-free filter paper (No. 40 Whatman, 11 cm.) by allowing 20–30 cc. of 0.5 *N* HCl to run through it. Place the Pt crucible contg. the partly ashed stool on a water bath and add 10 cc. of 0.5 *N* HCl. After it is hot transfer the ext. with a 10-cc. pipet to the washed filter paper, catching the filtrate in a 100-cc. flask. Repeat the procedure until the vol. is 100 cc. *Urine.*—Evap. a measured amt. of urine, 50 or 100 cc., in a Pt dish, ash, and ext. in the manner described for stool and make the ext. up to the original vol. of the urine. *Detn. of Na.*—Place 15–20 cc. of the stool ext. or 5–10 cc. of the urine ext. in a Pt dish and evap. to dryness. Transfer the ash to a graduated centrifuge tube with 2.5 cc. of 0.5 *N* HCl. Add 3 cc. of satd. $(NH_4)_2C_2O_4$ soln. and allow to stand for 10 min., thus pptg. practically all the Ca. Add concd. NH_4OH to 7 cc. and allow to stand for 45 min., thus pptg. the Mg. Centrifuge for 5 min. Transfer 5 cc. of the supernatant liquid to a Pt dish and evap. to dryness. Dry the residue thoroughly by placing the dish in an oven at 100° for a few min. Ash the sample by the method described above for 15–30 min., thus volatilizing all the NH_4 salts. Dissolve the small amt. of ash remaining in 2 cc. of 0.1 *N* HCl. Add a drop of phenolsulfonephthalein and make the soln. just alk. by adding 2–3 drops of 10% KOH. Add 10 cc. of $K_2H_2Sb_2O_7$ reagent *Detn. of* plete the analysis as previously described by T. and K. (*C. A.* **15**, 2461). in serum (*C.* The method is identical in principle with that described for the detn. of K 1912). Place the sample in graduated centrifuge tube which has been cleaned with a brush, washed out with strong cleaning fluid and thoroughly rinsed with distd. H_2O to prevent the ppt. from adhering to the sides of the tube. Add slowly, drop by drop, 1 cc. of the Na cobaltinitrite reagent, mix and allow to stand for $^1/_2$ hr. Make up to 5 cc. with H_2O, mix and centrifuge for $\frac{1}{4}$ min. at 1,300 r. p. m. Insert a 2-holed rubber stopper carrying a

short glass tube and a longer tube which reaches to about 3–4 mm. above the ppt., the end of the tube being drawn out to a bore of about 1 mm. and curved so that the opening is directed upward. Blow carefully through the short tube to remove all but 0.2–0.3 cc. of the supernatant fluid without disturbing the ppt. Run 5 cc. of H_2O down the side of the tube, hold the tube vertically and gently hit the lower end with a circular motion so as to mix the H_2O thoroughly with the residual reagent without disturbing the ppt. Centrifuge for 5 min. Repeat this procedure 3 times. Add an excess of 0.02 *N* $KMnO_4$ (generally 2–5 cc.) and 1 cc. of 4 *N* H_2SO_4. Mix thoroughly by means of a glass rod and place the tube in a boiling water bath. Examine the tube after 20–25 secs. and if the pink color has nearly disappeared, add more $KMnO_4$ from the microburet. 1 min. from the time the heating is begun the soln. should have a perfectly clear pink color. If not all the ppt. is oxidized, the contents will be cloudy and the color will fade; heating should then be continued until the soln. is clear and pink. Care must be taken not to heat too long, as a brown color develops and the sample must be discarded. Add 2 cc. of 0.01 *N* $Na_2C_2O_4$ promptly and mix. Add another 2 cc. if the $KMnO_4$ is not decolorized. Titrate the excess of oxalate with 0.02 *N* $KMnO_4$ delivered from a microburet, graduated in 0.2 cc., until a definite pink color is obtained which lasts for 1 min. Calcn.: [(total cc. of $KMnO_4$ used) − 0.03 (blank) × 2] − 2.0 (cc. of $Na_2C_2O_4$) × 0.071 = mg. of K in sample. The reagents are prepd. according to the methods previously described (*C. A.* **15**, 1912). *Detn. of Ca.*—Dil. 5 cc. of the stool ext. to 50 cc. with distd. H_2O and use 1–4 cc. for the detn. of Ca. Use an amt. of urine ext. corresponding to 1–4 cc. of urine. Measure the sample (usually 2 cc.) into a graduated centrifuge tube previously cleaned with cleaning mixt. and make up the vol. to 3–4 cc. with H_2O. Add a drop of phenolsulfonephthalein and 10% NH_4OH until the soln. is alk. Add approx. *N* H_2SO_4 until the soln. is just acid to redissolve any phosphates which may have been pptd. Add 1 cc. of approx. *N* $H_2C_2O_4$ and 1 cc. of a filtered satd. soln. of AcONa, drop by drop. Mix, allow to stand for ¾ hr. and centrifuge for 10 min. at 1,300 r. p. m. Complete the detn. as previously described for the estn. of Ca in serum (cf. preceding abst.). *Detn. of Mg.*—Place 25–50 cc. of the urine ext. or 10–30 cc. of stool ext. in a 100-cc. beaker. Add a drop of phenolsulfonephthalein and 10% NH_4OH until the soln. is just alk. Add 4 *N* H_2SO_4 until the soln. is acid and the phosphates are redissolved. Add 10 cc. of satd. $(NH_4)_2C_2O_4$ to the stool ext. or 5 cc. to the urine ext., mix and allow to stand for 15 min. Add 1 cc. of 10% $(NH_4)_2HPO_4$ and 5 cc. of concd. NH_4OH. Mix thoroughly, allow to stand for 1 hr. and filter through a 9-cm. No. 40 Whatman filter paper. Transfer the ppt. from the beaker with a rubber-tipped rod and 10% NH_4OH. Wash the paper 4 times with 30% alc. Transfer the paper with the ppt. to a 100-cc. beaker, add 30 cc. of warm H_2O and mix by use of a glass rod. Add 3 drops of tincture of cochineal (1 part of crushed cochineal digested with 10 parts of 25% alc.) and an excess of 0.1 *N* HCl (generally 5 cc.). After 5 min. titrate with 0.1 *N* NaOH delivered from a buret graduated in 0.05 cc. until the color changes from a light yellow to a purple. The end-point is very definite and 1 drop of the NaOH produces a decided change in color. Calcn.: cc. of HCl − cc. of NaOH × 1.21 = mg. of Mg in sample. A. P. Lothrop

The direct quantitative determination of sodium, potassium, calcium and magnesium in small amounts of blood. Benjamin Kramer and Frederick F. Tisdall. Johns Hopkins Univ. *J. Biol. Chem.* **48**, 223–32 (1921).—Na, K, Ca and Mg can be quant. detd. on only 7 cc. of blood by the methods described. Place 25 cc. of distd. H_2O in a 50-cc. volumetric flask and weigh. Obtain from 7.5–8 cc. of blood by means of a 10-cc. graduated syringe and add it slowly to the H_2O in the flask with continuous rotation. Weigh again. Add 1–2 drops of octyl alc. and 12–13 cc. of 12% CCl_3CO_2H while rotating the flask slowly. Add H_2O to the mark, mix, transfer to a large centri-

fuge tube and centrifuge for 5–10 min. at 1,000 r. p. m. Pour off the supernatant fluid, place an aliquot portion (usually 35 cc.) in a beaker and evap. If there are numerous particles of ppt. floating on the surface, allow the fluid to stand in the ice box for a few hrs. The fluid may be kept at this stage for at least 2 weeks before completing the detn. Dissolve the dry residue in 0.1 *N* HCl, transfer to a volumetric flask and make up to 10 cc. If the soln. is cloudy, centrifuge for a few min. and a clear straw-colored supernatant liquid will be obtained. *Detn. of Na.*—Place 4 cc. of the fluid in a Pt dish and evap. to about 2 cc. Add a drop of phenolsulfonephthalein and make the contents just alk. with 10% KOH (10–12 drops). Add 10 cc. of the $K_2H_2Sb_2O_7$ reagent followed by 3 cc. of 95% alc., added drop by drop while the specimen is stirred with a rubber-tipped rod. Allow to stand for 30 min., transfer to a weighed Gooch crucible and wash with 5–10 cc. of 30% alc. Place the crucible in a drying oven, gradually raise the temp. to 110° and dry at that temp. for 1 hr. Cool in a desiccator for 30 min. and weigh. Wt. of ppt. ÷ 11.08 = mg. Na in sample. The method of prepn. of the reagent and of the Gooch crucible, the precautions to be observed in the method and the care of the Pt have been previously described (*C. A.* **15**, 2461). *Detn. of K.*—Place 0.2 cc. of the material prepd. as outlined in a graduated centrifuge tube which has been cleaned with a brush, washed out with cleaning mixt. and thoroughly rinsed with distd. H_2O. Add 0.5 cc. of H_2O and 0.5 cc. of $NaNO_2$ soln. (15 g. of K-free $NaNO_2$, Merck, in 30 cc. of H_2O). Mix and allow to stand for 5 min. Add H_2O to 4 cc. and mix again. Add 2 cc. of the Na cobaltinitrite reagent, drop by drop. Mix and allow to stand for 30 min. Centrifuge for 7 min. at 1,300 r. p. m. and complete the detn. as described in the preceding abst. for the detn. of K in urine and stools. *Detn. of Ca.*—Place 4 cc. of the material prepd. as outlined in a cleaned, graduated centrifuge tube. Add 1 cc. of satd. $(NH_4)_2C_2O_4$ soln. and 2 cc. of a filtered satd. soln. of AcONa. Mix and allow to stand for 1 hr. Make up to 8 cc. with H_2O, mix, and centrifuge for 15 min. at 1,300 r. p. m. Save the supernatant liquid if Mg is to be detd. Complete the detn. as previously described (cf. preceding abst.). *Detn. of Mg.*—Measure 5 cc. of the supernatant fluid from the Ca detn. into a 30-cc. beaker and det. the Mg as described in the method for the estn. of Mg in serum or plasma (cf. preceding abst.). Calcn.: Reading (cc. of standard soln.) × 0.01 × 2 × (5/4) × 100 /(g. of blood used in the Ca detn.) = mg. of Mg in 100 g. of blood. *Concn. of Na, K, Ca, and Mg in human blood.*—Na, 170–225 mg.; K, 153–201 mg.; Ca, 5.3–6.8 mg.; Mg, 2.3–4 mg. per 100 cc. of blood. The concn. of these elements in normal blood varies more than in normal serum owing to variations in the corpuscular content of the blood. A. P. LOTHROP

A rapid method for the determination of hippuric acid in urine. F. B. KINGSBURY AND W. W. SWANSON. Univ. Minn. *J. Biol. Chem.* **48**, 13–20(1921).—The method requires about 2 hrs. for completion with normal urine and about 3 hrs. with urine contg. albumin and conserves the accuracy of the Folin-Flanders method. Treat 50 cc. of urine with 7.5 g. of NaOH and 0.5 g. of MgO in a 500–800 cc. Kjeldahl flask. Boil at such a rate as to bring the vol. down to 25 cc. in 1/2 hr. While the mixt. is still at the boiling temp. add 1 cc. of a 7% $KMnO_4$ soln., taking care to wash down any that remains in the neck of the flask with the smallest amt. of H_2O possible. Twirl the flask gently for 1–2 min., cool under the tap, place a fairly closely fitting test-tube condenser in the neck and slowly pour down the side of the condenser 30 cc. of cond. HNO_3. Gently boil for 45 min. with a good current of H_2O flowing through the condenser, then cool under the tap. Rinse down the condenser with 25 cc. of H_2O to remove any $C_6H_5CO_2H$ sublimed on the bottom, then transfer the contents of the flask to a 500-cc. separatory funnel contg. 25 g. of solid $(NH_4)_2SO_4$. Rinse the flask with 25 cc. of H_2O. After the $(NH_4)_2SO_4$ has dissolved, ext. the $C_6H_5CO_2H$ successively with one 50-cc., one 35-cc., and two 25-cc. portions of neutral, well-washed $CHCl_3$, using the first 2 portions to

rinse the Kjeldahl flask. Combine the exts. in a second separatory funnel and wash once with 100 cc. of the Folin-Flanders salt soln. (1 cc. of concd. HCl in 2 l. of satd. NaCl soln.). Draw off through a dry filter paper into a dry Erlenmeyer flask. Rinse the separatory funnel with 20 cc. of $CHCl_3$, drawing it off into a small beaker to which the wet filter paper has been transferred. Rinse the paper with the $CHCl_3$ and pour the rinsing through a dry filter into the bulk of ext. in the Erlenmeyer flask. Add 4 drops of a 1% soln. of phenolphthalein in abs. alc. and titrate the $C_4H_4CO_2H$ soln. to faint but definite pink with 0.1 *N* EtONa soln. prepd. and standardized according to the method of Folin and Flanders (*C. A.* **6**, 2245). The *neutral* $CHCl_3$ is prepd. as follows: Wash U. S. P. $CHCl_3$ twice with an equal vol. of distd. H_2O. If the $CHCl_3$ has been used in analyses and, therefore, contains $C_4H_4CO_2Na$ and alc., filter through a dry paper and wash successively with equal vols. of tap H_2O, once; tap H_2O contg. 5–10 cc. of satd. NaOH, twice; tap H_2O, twice; distd. H_2O, once; Shake 155 cc. of the $CHCl_3$, the amt. used in the analysis, with dil. HNO_3, wash with 100 cc. of the Folin-Flanders salt soln., filter through a dry paper and titrate; not more than 0.1 cc. of 0.1 *N* EtONa soln. should be needed for the titration of this amt. of $CHCl_3$. A. P. LOTHROP

A possible source of error in testing for Bence-Jones protein. C. W. MILLER AND J. E. SWEET. Univ. Pa. *J. Biol. Chem.* **48**, 21–2(1921).—If urine, especially of dogs, contg. a small amt. of serum albumin is allowed to stand at room temp. for 8–24 hrs. after voiding, a positive heat coagulation test will occasionally become less marked on standing or even disappear entirely, but a cloudiness will still be produced with $K_4Fe(CN)_6$ and AcOH. The change is apparently due to a proteolytic enzyme in the urine. It is obvious, therefore, that fresh urine should be used in testing for Bence-Jones protein. Slightly contaminated urine from the cage may often contain enough digestion products to give Bence-Jones reactions when such reactions were negative in catheterized specimens. Emulsified C_7H_8 may also be confusing because the cloudiness disappears on heating and immediately returns on cooling; this reaction, however, can be easily differentiated by confirmatory tests. A. P. LOTHROP

A method for the determination of sugar in normal urine. STANLEY R. BENEDICT AND EMIL OSTERBERG. Cornell Univ. Med. College. *J. Biol. Chem.* **48**, 51–7(1921); cf. *C. A.* **12**, 1304; **15**, 2463.—The color due to the interaction of creatinine and picric acid in the presence of NaOH is destroyed by the addition of Me_2CO without serious effect on the color developed through the action of the sugar. Dil. the urine so that the sp. gr. does not exceed 1.025–1.030 and treat 15 cc. with 1 g. bone-black, purified as described below. Shake vigorously occasionally for 5–10 min. Filter through a small dry filter into a dry flask or beaker. One to 2 cc., not over 3 cc., of the filtrate should be used for the detn.; the vol. used should contain about 1 mg. of sugar Measure the proper vol. into a large test-tube graduated at 25 cc. and add H_2O to make the vol. exactly 3 cc. Add exactly 1 cc. of 0.6% picric acid soln. (best prepd. from dry picric acid) and 0.5 cc. of 5% NaOH soln. Just before the tube is ready to be placed in boiling H_2O add 5 drops of 50% Me_2CO (prepd. fresh every day or two), taking care that the drops fall into the soln. and not on the sides of the tube. Shake gently to mix the contents, place immediately in boiling H_2O and leave for 12–15 min. Prep. the standard simultaneously by treating 3 cc. of pure glucose soln. (contg. 1 mg. of sugar) exactly as described for the unknown and heating simultaneously. The glucose soln. contg. 1 mg. per 3 cc. will keep indefinitely if preserved with C_7H_8. Make up to 25 cc. and read in a colorimeter. The amt. of picric acid soln. must be measured with exactness but the alkali may be measured by adding about 10 drops to each of the tubes from the same pipet. An unknown contg. between 0.75–1.75 mg. can be estd. with the 1 mg. standard. If less than 0.7 mg. of sugar is present in the unknown, use a standard contg. 0.5 mg. of sugar in 3 cc. and dil. to 12.5 instead of to 25 cc. The method is

accurate for both unfermented and fermented urines and there is excellent agreement between it and the original $Hg(NO_3)_2$ method. For clinical purposes the bone-black may be omitted as the results will be only 0.03–0.04% too high. *Purification of bone-black.*—Treat 250 g. of com. bone-black with 1.5 l. dil. HCl (1 vol. of concd. acid dild. with 4 vols. of H_2O) and boil for 30 min. Filter on a large Büchner funnel and wash with hot H_2O until the washings are neutral to litmus. Dry and powder. Do not use the highly absorbent animal charcoals on the market in this connection. Test the final product by shaking 15 cc. of a glucose soln. containing 1 mg. of sugar per 2 cc. of H_2O with 1 g. of the bone-black and detg. the sugar in the filtrate; there should be no detectable absorption of the sugar. A. P. Lothrop

The estimation of creatinine in the presence of acetone and diacetic acid. Nathan F. Blau. Cornell Univ. Med. College and Bellevue Hosp. *J. Biol. Chem.* **48**, 105–18 (1921).—Me_2CO, Et acetoacetate, and diacetic acid interfere with the colorimetric detn. of creatinine in pure soln. as well as in urine. Me_2CO has a fading effect, which, however, does not become marked until the concn. reaches 0.7%; diacetic acid in concns. of 0.015–0.02% causes a perceptible fading, which becomes progressively greater as the concn. of the acid or the time the test is allowed to stand are increased. The diacetic acid can be removed from urine by boiling it with H_2O but when this method is used occasional irregularities occur. In the method described the urine is boiled with a substance, MeOH, which lowers the b. p. and at the same time has no effect on either creatine or creatinine. Measure 10 cc. of urine into a 300-cc. flask contg. a few glass beads. If the urine is alk., adjust the reaction with concd. HCl so that it reacts red to *litmus but not blue* to Congo red. Add 5 vols. of MeOH and slowly boil the mixt. over an asbestos mat until 1–2 min. after the temp. has risen *to 100°; this should* take not less than 15 min. (The MeOH can be recovered by distg. and purified by refluxing with acid $HgSO_4$, filtering off the ppt. formed and fractionating the filtrate.) Thoroughly cool in running H_2O, add 15 cc. of satd. picric acid and 5 cc. of 10% NaOH. Allow to stand for 8 min., wash quant. into a 500-cc. flask, dil. to the mark and read in a colorimeter. Ten cc. of urine contg. as much as 0.7% of diacetic acid can be freed from the acid by this method if the liquid is kept actively boiling during the entire 15 min. A. P. Lothrop

Creatinine and creatine in muscle extracts. I. A comparison of the picric acid and the tungstic acid methods of deproteinization. Frederick S. Hammett. Wistar Inst. *J. Biol. Chem.* **48**, 127–31(1921).—Concordant results were obtained in the detn. of muscle creatinine, preformed and total, whether the muscle exts. were deproteinized with picric or tungstic acid. A freshly satd. soln. of purified picric acid was always used and a series of standards were always available so that there would be one with which the unknown would closely correspond. When creatine and creatinine alone are to be detd. in tissue exts., the picric acid pptn. is especially convenient because that method requires less manipulation. A. P. Lothrop

The preparation and standardization of collodion membranes. Arnold H. Eggerth. New York. *J. Biol. Chem.* **48**, 203–21(1921).—A graded series of collodion membranes of a wide range of permeability can be prepd. by varying the proportion of alc. and Et_2O in the solvent in which the pyroxylin is dissolved. The pyroxylin used was that manufd. by the duPont de Nemours and Co. under the name of "parlodion"; all the solns. contained 6 g. in 100 g. of the alc.-Et_2O solvent. The alc. used was distd. over CaO and redistd. over Na and the Et_2O was distd. over Na. Alc.-Et_2O mixts. contg. 20–80 parts of alc. by wt. readily dissolve 6% parlodion; to obtain solns. contg. 10, 15, 85, and 90 parts of alc. it is necessary first to make a thick soln. of the collodion in a portion of the solvents and later add the alc. or Et_2O as the case may be. Only 2% of moisture sets the 90 alc. soln. to a firm gel but the Et_2O-rich solns. are

made more fluid by H_2O. The method of prepn. of the membranes is given in detail. The following test substances were used in detg. the permeability of the membranes: 2% NaCl, 0.2 *M* KH_2PO_4, 20% sucrose, 8% raffinose, 0.2% indigo carmine, 1% safranine, 1% primary proteose at p_H 7, dialyzed serum protein, oxyhemoglobin, CO-hemoglobin, metbemoglobin and 1% Congo red. With all these substances the permeability increased with the alc. content of the membrane. With the various hemoglobins, indigo carmine and safranine the speed of diffusion increased up to a certain point, above which the diffusion was limited only by the diffusion const. of the substance in H_2O. No dialysis occurred with soln. of the hemoglobins, primary, proteose, serum or Congo red with membranes containing less than 40% of alc. 1% Congo red exerts an osmotic pressure, causing a marked increase in the vol. of the dialyzate. The conclusions of Walpole (*C. A.* 9, 3253) and of Brown (*C. A.* 10, 1360; 11, 2912) that the ratio of the dry to wet wt. of a membrane is an index of its permeability was confirmed; this ratio varied from 1.73 in the 10 alc. membrane to 9.2 in the 90 alc. Membranes can be prepd. for use in bacteriology and serology which will allow passage of proteins after sterilization if an 80 alc. soln. is used. If autoclaved at 20 lbs. pressure for 30 min., they shrink over 50% in vol.; the shrinkage is about 33% after 3 steamings in an Arnold sterilizer. Such membranes are serviceable and strong and will stand a pressure of 25 cm. of Hg. *Staphylococcus aureus* was grown in such sterile membranes for 2 months without contaminating the surrounding broth. *B. influenzae* was grown in plain broth without hemoglobin by growing it on the inside of a sterilized sac with a living culture of staphylococcus, streptococcus, or pneumococcus growing on the outside; controls without the symbiotic organisms showed no growth of *B. influenzae*. It is possible thus to study symbiosis of organisms while keeping each in pure culture. Addition of 10–30% of lactic acid to the alc.-Et_2O soln. (50–80% alc.) greatly increases the permeability of the membrane; 10–20% of AcOH gives added durability and elasticity but makes the membrane somewhat less permeable. Glycerol and H_2O increase permeability but neither are as effective as lactic acid. A. P. Lothrop

C—BACTERIOLOGY

A. K. BALLS

The presence of calcium carbonate in a group of sulfur bacteria. Egon Bersa. Univ. Grāz. *Sits. Akad. Wiss. Wien, Abt. I*, 129, 231–57(1920).—*Achromatium* Schewiakoff was found to be identical with *Modderula* Frenzel and *Hillhousia* West and Griffiths; the dimensions vary from 9–75μ × 9–25μ; the plasma is coarse and contains vacuoles; there is no nucleus but small chromatin-like granules are present; the membrane which is fairly strong contains no cellulose and is probably a modified tough protoplasmic skin. The cell is surrounded by a layer of mucus which is probably elaborated through the membrane by the cell. The motility is very irregular and slow with no organs of locomotion; reproduction is by simple fission. The honeycomb structure of S granules increases and decreases in proportion to the H_2S content of the water. Granules of amorphous $CaCO_3$ (2–12μ) are present in the vacuoles and are surrounded by a thin membrane; the physiol. significance as well as the reason for their appearance and disappearance is as yet unknown. In *Pseudomonas hyalina*, $CaCO_3$ was found to be the sole ingredient, S being absent. All three organisms owe their appearance to the presence of H_2S and belong therefore to the S bacteria of which they probably form a particular group. N. A. Langr

A new modification and application of the Gram stain. G. J. Hucker. *J. Bact.* 6, 395–7(1921).—The stain is made as follows: (1) Gentian violet soln.; aniline oil 3 cc., abs. alc. 7 cc., water 90 cc., shake, filter, and add gentian violet 2 cc. (2) Iodine soln.; iodine 1 g., KI 2 g., water 300 cc. (3) Decolorizing soln.; aniline oil 2 parts,

xylene 1 part, use 5 parts of this mixt. and 95 parts of 95% alc. (4) Counterstain; Bismarck brown 4.5 g., water (boiling) 50 cc., filter, and add 30 cc. of 95% alc. This is especially applicable to smears of milk. 0.001 cc. of milk is spread on a slide over an area of 1 sq. cm. The fat is removed with xylene, the slide fixed in 95% alc. for 2 minutes, blotted and placed in the gentian violet soln. for 45 sec., immersed in the iodine soln. 1 min., destained in the decolorizing soln. until no more color can be removed, and counterstained for 45 seconds. JOHN T. MYERS

The growth and the proteolytic enzymes of certain anaerobes. K. G. DERNBY AND J. BLANC. Pasteur Institute. *J. Bact.* 6, 419–30(1921).—The optimal and minima H-ion concns. for the growth of the anaerobes *Clostridium sporogenes*, *C. histolyticum*, *C. canadiense*, *C. putrificum* and *C. perfringens* have been detd. The range in which all these organisms live has the limits p_H 5 to 9. The optimal range for all seems to be at or about p_H 7 and is apparently a rather broad one. The proteolytic activities of filtrates from *Clostridium sporogenes* and *C. histolyticum* has been studied. Gelatin is liquefied and peptone disintegrated in the range p_H 4 to 8, and optimum for both these reactions seems to be about p_H 6. It is evident that the filtrates contain a tryptase. JOHN T. MYERS

A new method for the staining of bacterial flagella. H. G. PLIMMER AND S. G. PAINE. *J. Path. Bact.* 24, 286–8(1921).—The stain is made as follows: Tannic acid 10 g., $AlCl_3.6H_2O$ 18 g., $ZnCl_2$ 10 g., rosaniline-HCl 1.5 g. and 60% alc. 40 cc. The solids are triturated with the alc. forming a stain which is stable for several years. This mordant is applied to the film without fixation as follows. One part of the stain is shaken for 1 minute with 4 parts of water, and filtered on to the slide. After one minute it is rapidly washed off and the slide flooded with cold carbolfuchsin, when it is ready for mounting. JOHN T. MYERS

Microörganisms and some of their industrial relations (CHAPMAN) 16.

D—BOTANY

CARL L. ALSBERG

Injuries to crops and vegetation due to fumes from carbide and aluminium factories. LEOPOLD WILK. *Arch. Chem. Mikros.* 9, 176–89(1916).—Report of a detailed investigation. The gases from the carbide and Al factories were found to retard or utterly destroy the power of the leaf of absorbing CO_2. The gases and smoke from the CaC_2 factory were found to contain CaO, CaC_2, C_2H_2, PH_3, AsH_3, H_2S and NH_3. Many of these latter gases are due to the effect of dew or moisture on the CaC_2 smoke. The fumes from the Al factory are composed largely of finely divided C which covers the leaves of trees, etc., and hinders "breathing." The destruction of vegetation extended over an area of several sq. miles. C. G. F.

The mutual precipitation of dyes and plant mucilages. F. E. LLOYD. McGill Univ. *Trans. Roy. Soc. Canada* 14, Sect. V, 23–31(1920).—Effects of various dyes have been tested on the mucilages of cacti (*Opuntia*) and of flax (*Linum*). Those dyes (ruthenium red, neutral red, vesuvin, gentian violet, methylene blue and safranine) which are adsorbed by such mucilages lower their viscidities with a vigor directly related to the rapidity of adsorption. Fuchsin, erythrosin, corallin, orange G, and methyl orange are not adsorbed. The change in viscidity is due to mutual pptn. When the dye is in insufficient quantity partial coagulation (flocculation) accompanied by slight lowering of viscidity occurs. When the dye is in sufficient quantity a continuous coagulum is formed within which the viscidity is raised by syneresis. The observations suggest possible methods of identification of substances of carbohydrate nature occurring in plant tissues, and can perhaps be applied to the action of intravitam stains as methylene blue. A. T. CAMERON

The law of the threshold of stimulation. A. PÜTTER. *Naturwissenschaften* **8**, 501–7(1920).—A survey of the status of knowledge concerning the threshold of stimulation acquired through physicochem. analysis. The characteristics of and differences between light and elec. stimuli are outlined, with a discussion of the Nernst and Hill formulas for elec. stimuli and that of P. for light. No formula has yet been devized to express a general law for the threshold of stimulation, and specific equations for various types of stimuli are necessary. In general stimuli effective instantly for the plant at full strength, such as light, gravity and electricity are classed together. Likewise stimuli which are a function of time, *i. e.*, effective only after diffusion, such as chem., osmotic and thermal, are classed together separately from the former. It is maintained that the conditions necessary for the threshold of stimulation are "a sensitivity in a living system where in the system or at a certain location in it the concn. of specific active substances reach in a definite time a certain magnitude which is const. for the different systems and different stimuli." C. C. DAVIS

The superfluousness of manganese for the oxidase molecule in the cultivation of Hedera helix, and Bertrand's manganese theory of the oxidases. A. W. VAN DER HAAR. *Biochem. Z.* **113**, 19–28(1921); cf. *C. A.* **15**, 1554.—Since 11. found 0.005 mg. instead of 0.05 mg. of Mn in the whole ash of one plant, as the first abstract stated, it is not considered possible by him that such a trace can be of significance. F. S. HAMMETT

Carrageen (Chondrus crispus). II. The occurrence of ethereal sulfates in the plant. PAUL HAAS. University College, London. *Biochem. J.* **15**, 469–76(1921); cf. *Ann. Applied Biol.* **7**, 352(1921).—Carrageenin is Irish moss mucilage. An aq. ext. of carrageenin gives the reaction of the Ca but not the SO_4 ion; after hydrolysis the latter also may be detected. "The $CaSO_4$ obtained by incineration is not present in the plant as such, but is produced by the decompn. of an ethereal sulfate pre-existing in the undecomposed material." The formula assigned is $R(OSO_2O)_2Ca$. In support of this structure, it is shown that the amt. of sulfate in soln. after hydrolysis is double that found in the ash. On incineration, the compd. loses one-half its S as H_2SO_4 and the other half is converted to $CaSO_4$. "The present instance appears to be the first recorded case of the existence of carbohydrate esters of sulfuric acid among plant products." BENJAMIN HARROW

The nature and composition of Irish moss mucilage. PAUL HAAS. *Pharm. J.* **106**, 485(1921). Irish moss mucilage replaced gelatin with apparent success in the invalid dietary of Malta hospitals during the war. Still, *in vitro*, digestive juices show little action upon it, at least at blood heat. At 50°, saliva, also HCl of gastric juice concn. produce a certain amt. of hydrolysis. With 5% citric acid on a boiling water-bath, carrageenin loses its gelatinizing power after a few min. Unlike gelatin, carrageenin retains its viscosity while hot. Haas and Hill (*Annals of Applied Biology* **7**, 352 (1921)) find material differences between the cold H_2O ext. (*C. E.*) and the subsequent hot H_2O ext. (*H. E.*). Dried *C. E.* contains much ash, partly removable by dialysis; the remainder, 20%, is in chem. combination. *H. E.* contains 17.5% of the combined ash constituent. Codliver-oil emulsion with dialyzed *H. E.* is very stable, that with *C. E.* (equiv. strength) is quite unstable; that with ordinary hot H_2O ext. has intermediate stability. Differences in the emulsifying power of various samples are probably due to variation in the proportion of *H. E.* present. A 1% soln. of *H. E.* in hot H_2O gelatinizes on cooling; a 3% soln. makes a fairly stiff jelly, a 5% soln. a jelly m. 41°, thus rendering it useful for solid culture media at or slightly above the blood heat. Cf. preceding abst. S. WALDBOTT

"Fumed" oak and natural brown oak. C. K. TINKLER. King's College for Women, London. *Biochem. J.* **15**, 477–86(1921).—The brown coloration on "fumed" oak is

due to the combined action of NH_3 and atm. O. Although a color similar to that of natural brown oak can be obtained by the action of NH_3 or a substituted ammonia on English oak under certain conditions, the production of this color in nature is probably not entirely dependent on the nitrogenous constituents of wood. BENJAMIN HARROW

After-ripening and germination of juniperus seeds. D. A. PACK. *Botan. Gaz.* 71, 32–60(1921).—This research is in answer to inquiries by various growers as to the best methods of handling juniper seeds. After-ripening occurs at temps. between −1° and 10°, although fastest at about 5°. The changes that accompany after-ripening at 5° are: (1) A rather rapid and complete inhibition, followed by a steady decrease in water content during after-ripening or until near germination; (2) increased H-ion concn., especially of the embryo; (3) an increase in titratable acid; (4) a steady increase in the degree of dispersion of the stored fat; (5) decrease in the amt. of stored fat and protein, with an increase of the sugar content and the first appearance of starch; (6) the translocation of food in the form of fat or fatty acid from endosperm to embryo; (7) a seven-fold increase in the amino-acid content, and a complete disappearance of histidine from the endosperm; (8) an increase of sol. proteins, with a marked hydrolysis of the stored proteins; (9) slight growth of embryo; (10) very slight increase of the respiration intensity; (11) increased respiratory quotient; (12) decreased intramol. respiration; (13) doubling of the catalase activity; and (14) the rise in vigor of seeds as shown by their resistance to fungal attack. The changes accompanying the after-ripening of dormant seeds are represented by the accumulation of cell-building materials; acids, phosphatides, active reducing substances, sol. sugars, pentoses, amino acids, etc.; the dispersion of material; and the transformation of storage materials. BENJAMIN HARROW

The ash picture and plant relationship. HANS MOLISCH. Univ. Vienna. *Sits. Akad. Wiss. Wien, Abt. I*, 129, 261–93(1920).—The ash picture or "spodogram" is as characteristic for many plants as the leaf form, the number of petals or the structure of the seed pod. The material to be investigated is ignited in an open porcelain crucible until the ash is white, cooled, a portion transferred to a glass slide, treated with a drop of $PhNH_2$ and covered with a cover glass. PhOH or Canada balsam diluted with $(C_6H_4)Me_2$ may be used in place of $PhNH_2$. Many cell structures are left intact after ignition and identification is thus possible. To det. the SiO_2 structures, the material on the slide is first treated with 20% HCl to dissolve the carbonates; doubtful cases may be treated with a H_2SO_4-$K_2Cr_2O_7$ mixt. which dissolves all the org. substances. All ashes may be permanently mounted in Canada balsam which has been made mobile with C_6H_4-Me_2. Both fresh and old plant material may be used. This method may be used in classification, identification and adulteration work. Spodograms of members of the Lycopodiaceae, Equisetaceae, Gramineae, Cyperaceae, Orchidaceae, Marantaceae, Musaceae, Zingiberaceae, Palmae, Pandanaceae are described and some microphotographs are reproduced. N. A. LANGE

The narrow-leaved milkweed (Asclepias mexicana) and the broad-leaved or showy milkweed (Asclepias speciosa), plants poisonous to live stock in Nevada. C. E. FLEMING, N. F. PETERSON, M. R. MILLER, L. R. VAWTER AND L. H. WRIGHT. Univ. Nevada Agr. Expt. Sta., *Bull.* 99, 1–32(1920).—Successive exts. of *A. mexicana* with benzene, Et_2O, $CHCl_3$, Et acetate and EtOH were non-toxic with the exception of the benzene. Exts. of the original dry powder showed the presence of alkaloids with all the alkaloidal reagents used. The active principle of *A. mexicana* apparently differs from that of *A. galioides*. ALBERT R. MERZ

The poison parsnip or water hemlock (Cicuta occidentalis), a plant deadly to live stock in Nevada. C. E. FLEMING, N. F. PETERSON, M. R. MILLER, L. H. WRIGHT AND R. C. LOUCK. Univ. Nevada Agr. Expt. Sta., *Bull.* 100, 1–23(1920).—The active

principle (cicutoxin, $C_{15}H_{20}O_3$) dissolves in Et_2O, EtOH, MeOH, Me_2CO and $CHCl_3$ and is insol. in H_2O, glycerol and $PhNH_2$. It is a viscous yellowish liquid constituting 0.3–0.4% of the green tubers, and changes spontaneously to a semi-solid ruby-red or reddish brown substance. ALBERT R. MERZ

Death camas (Zygadenus paniculatus and Zygadenus venenosus), plants poisonous to sheep and cattle. C. E. FLEMING, N. F. PETERSON, M. R. MILLER AND L. H. WRIGHT. Univ. Nevada Agr. Expt. Sta., *Bull.* 101, 1–31(1921).—The "Z-alkaloid" of *Z. paniculatus* constitutes approx. 0.3% of the dried plant, is sol. in EtOH, MeOH, $CHCl_3$ and Me_2CO and to a less degree in benzene and CCl_4, and resinifies to a white substance on standing without change of toxicity or soly. On long standing 1% of the total seps. out as an alc.-insol., cryst. material. "Z-alkaloid" does not appear to be the same as the zygadenin obtained from *Z. intermedius*. ALBERT R. MERZ

E—NUTRITION

PHILIP B. HAWK

NORMAL

Present position of vitamines in clinical medicine. H. CHICK AND E. J. DALZELL. *Brit. Med. J.* 1920, II, 151–4.—The quantity of vitamine must be considered in a diet. Although present the amt. may be insufficient. Charts are included showing the improvement effected by adding substances contg. vitamine to the diet of breast-fed and artificially fed children. A. T. CAMERON

Feeding experiments in connection with vitamines A and B: I. The value of steam-distilled palm-kernel oil as a control fat. II. Wheat bran as a source of vitamines A and B. A. D. STAMMERS. Nutrition Lab., Port Sunlight, Eng. *Biochem. J.* 15, 489–93(1921).—Palm-kernel oil, steam distd. for 3–4 hrs. at 230° to 260° is entirely deprived of vitamine A. Bran is known to contain vitamine B, but a test was now made to show whether it contained vitamine A. Three sets of 8 rats were fed on (*a*) basal diet, steam-distd. palm-kernel oil and wheat bran; (*b*) basal diet, butter fat and wheat bran; (*c*) basal diet and butter fat. In (*a*) and (*b*) no antineuritic was given, (*c*) received a marmite ext. The basal dietary consisted of purified caseinogen 26, starch 54, cane sugar 15, salt 5. The caseinogen was prepd. by spreading out com. casein in a hot-air chamber for some hrs., and subsequently extg. with hot alc. The salt mixt. used was based on McCollum's formulas as modified by Hopkins: NaCl 46.25, $MgSO_4$ 71.2, NaH_2PO_4 92.68, K_2HPO_4 254.6, $CaH_4(PO_4)_2.2H_2O$ 144.2, Ca lactate 347, ferric citrate 31.52, NaF 0.55, $MgSO_4$ 2.00, KI 10.00. The marmite ext. was prepd. by shaking 250 g. of crude marmite with 2 l. 80% alc. for 2 hrs. The liquid was decanted and filtered into a distg. flask, and the alc. evapd. under reduced pressure. The resulting fluid was filtered and made up to 250 cc. with distd. water. Each animal received 2 cc. of this per day. The expts. lasted 3 months. The av. wt. of the rats at commencement was 45–47 g. At the conclusion, the rats in class *b* averaged 133 g.; in class *c* 120.5 g., and in class *a* 112 g. The growth recorded was far below the normal. The bran may, therefore, be regarded as contg. vitamine A. Though the growth of the animals was subnormal, there was no sign of deficiency disease. B. H.

Vitamines in milk. M. J. ROSENAU. Boston. *Boston Med. and Surg. J.* 184, 455–8(1921).—Milk contains the 3 vitamines, fat-sol. A, H_2O-sol. B, and antiscorbutic vitamine C. Fat-sol. A and H_2O-sol. B are resistant to heat, while vitamine C may be influenced by heat, depending on conditions. Canned milk and dried milk contain the first 2 vitamines in almost their original potency. The amt. of vitamine C in canned milk will vary with many factors, primarily, with the amt. in the original milk, and secondarily, with the process of heating and evapn., with special reference to oxidation. JULIAN H. LEWIS

ABNORMAL

Report of a committee of inquiry regarding the prevalence of pellagra among Turkish prisoners of war. *J. Roy. Army Med. Corps* 33, 426–47, 508–27(1919); 34, 70–9, 173–84, 272–92(1920).—The disease investigated was true pellagra; infection took place generally prior to capture. No evidence relating to the etiology of the disease to bacteria, protozoa, blood conditions, pathology, or any other factor than diet has been obtained. It is considered that lack of sufficient biological value of protein stands in etiological relation to the disease, certainly as an exciting, and possibly as a detg. factor. The pellagrin suffers from loss of appetite, deficiency of gastric HCl, and hence, with accompanying malassimilation of fat, loss of protein through malassimilation, bacterial putrefaction (that of tryptophan is greater than normal), and diarrhea. This loss may convert a diet adequate in protein for normal persons into one inadequate for pellagrins. Latent pellagrins with deranged digestion and deficient power of assimilation, due to insufficient protein diet before capture (captured documentary evidence showed that such deficiency existed), while remaining apparently healthy when at rest, may very rapidly develop into clinical pellagrins when employed at work, through inability to assimilate the extra food given in a form suitable to provide the additional energy output required. The clinical features of the disease are those of a profound adrenal inadequacy, but there is not sufficient evidence to show how this is produced. There is some evidence that a mild acidosis may be a metabolic accompaniment. Of 60 autopsies on pellagrins, in only 2 could pellagra be regarded as the detg. cause of death. Postmortem examn. of different prisoners dead from various diseases suggested that they had suffered from such food deficiency; that the adrenals of all were abnormal, though only those who developed lesions of the sympathetic nervous system showed symptoms of pellagra. No officer and no German prisoner developed pellagra. A. T. CAMERON

Basal metabolism and its clinical application. JOSEPH S. HEPBURN AND H. M. EBERHARD. Hahnemann Med. Coll., Phila. *J. Am. Inst. Homeopathy* 14, 231–7 (1921).—The various methods for the detn. of basal metabolism are described, and results obtained with the metabolimeter of Jones are reported. A case of hypothyroidism with a basal metabolic rate of −16.3% was restored to a normal rate by administration of desiccated thyroid. A case of hyperthyroidism had a rate of +35.4% after operation on the thyroid. Two weeks after X-ray treatment the rate had risen to +58.7%; and it decreased to +35.4% at the end of another week. A second X-ray treatment was then given; 1 week later the rate was +45.7%; at the end of a further period of 2 weeks it had decreased to +17%. Hence exposure of the thyroid to the X-ray produced first an increase, then a gradual decrease in the basal metabolic rate.
JOSEPH S. HEPBURN

F—PHYSIOLOGY

ANDREW HUNTER

Physiological cost of muscular work measured by the exhalation of carbon dioxide. A. D. WALLER AND MISS G. DE DECKER. *Brit. Med. J.* 1921, I, 669–71.—Tables are given for colliers and shoemakers. Summarizing these with previous results, the figures for cc. CO_2 per sec. are, for sedentary work, below 5; light work, 5–10; medium, 10–15; heavy, 15–20; heaviest, over 20. The corresponding cal. per hr. are 20 times these figures. A. T. CAMERON

Physiological cost of muscular work. L. HILL AND J. A. C. CAMPBELL. *Brit. Med. J.* 1921, I, 733–4.—Criticism of Waller and De Decker's method (preceding abst.). The half-min. measurements are considered as too short for accuracy. Insufficient emphasis is placed on diet. A. T. CAMERON

Estimation of the physiological cost of muscular work. J. B. Orr and J. P. Kinloch. Aberdeen. *Brit. Med. J.* 1921, II, 39–40.—Waller's method has an inherent source of error, in neglect of the significance of the respiratory quotient in detg. the caloric equiv. of the vol. of CO_2 exhaled. A. T. Cameron

Presence in urine of a nitrogenous residue not estimable by Kjeldahl's method. Comparable study of results furnished by the Kjeldahl-Foerster technic and the Dumas Method. W. Mestrezat and Martiie P. Janet. *Bull. soc. chim. biol.* 3, 88–94 (1921).—Foerster's modification gives slightly higher results for urine-N than the modifications of Hoppe-Seyler and Krüger. In a comparison of the first procedure with the dry method of Dumas the latter gave invariably higher values, one to 5% in normal urine, and even 9.7% in pathol. urines after purgation. There exists, therefore, a N-fraction in urine not usually broken up by heating with H_2SO_4 and probably present in a heterocyclic compd. Sadikoff (*Z. physiol. Chem.* 39, 396(1903)) found similar discrepancies when using the 2 methods for animal collagens. A. T. Cameron

Chemical study of amniotic liquid. R. Clogne and J. Réglade. Paris. *Bull. soc. chim. biol.* 3, 279–82(1921).—No oxidases nor reductases were found in 20 normal specimens. Total solids were 10.85 to 14.50%, mean of 12 analyses, 12.36. Urea, measured accurately by the xanthydrol method, varied between 0.16 and 0.31 g. per l., with a mean value of 0.23 (23 normal cases); measured by the hypobromite method the corresponding figures were 0.25, 0.55 and 0.31. Previous observers with similar inaccurate methods obtained even higher figures. Urine of the new-born, where measured, showed a much higher urea content than the corresponding amniotic fluid. This difference may have a bearing on the problem of the origin of the amniotic fluid. A. T. C.

Degradation of valeric acid in the animal organism. L. Blum and E. Aubel. Strasbourg. *Bull. soc. chim. biol.* 3, 307–10(1921).—Injection intravenously into rabbits of Na valerate gave no acetone bodies in the urine (confirmatory of Embden and Marx; Baer and Blum). Along with undestroyed valeric acid, *d*-lactic and pyruvic acids were found in the urine. The results afford a further illustration of the oxidation of fatty acids by steps involving the removal of 2 C atoms. A. T. Cameron

Pituitrin-like substance in cerebrospinal fluid. W. E. Dixon and D. Cow. *Proc. Roy. Soc. Med.* 14, Sect. Ther. and Pharm., 6(1921).—Normal cerebrospinal fluid has no pituitrin action; after injection of exts. of intestinal mucous or ovary it appears after an hr. to contain a substance with the properties of pituitrin. After injection of pituitary ext., the fluid gave the pituitrin effect immediately. Exts. of testis, epididymis, liver, pancreas choroid plexus, etc., histamine, pilocarpine, and adrenaline had no effect. A. T. Cameron

Chemical factors in fatigue. I. The effect of muscular exercise upon certain common blood constituents. Norris W. Rakestraw. Stanford Univ. *J. Biol. Chem.* 47, 565–90(1921).—Fatigue was induced in 21 subjects by (*A*) having them run up and down stairs for not more than 15 min. or (*B*) by having them ride a bicycle for 2 or 3 hrs. Before and after the exercise, samples of blood were taken and the whole blood and plasma analyzed and values for the corpuscles calcd. from these results and the hematocrit reading. *A* increased the blood-sugar concn. both in plasma (91 to 126 mg.) and in corpuscles (102 to 134); while *B* was followed by a drop in blood sugar, greater in plasma (96 to 81) than in whole blood (99 to 94). Both kinds of exercise were followed by an increased concn. of uric acid; plasma, 4.6 to 5.7 mg.; whole blood, 4.1 to 4.7 mg. *A* had no effect on the urea or non-protein N but *B* increased both slightly: urea N, 20.5 to 21.7 in plasma, 19.2 to 20.9 in whole blood; non-protein N, 27.3 to 29.7 in plasma, 38.6 to 41.7 in whole blood. Neither *A* nor *B* appreciably affected the concn. of preformed or total creatinine. Both forms of exercise slightly, though irregularly lowered the concn. of cholesterol, particularly in the corpuscles (163 to 154 mg.). There was

a slight increase in sp. gr. (Westphal balance), in viscosity and in hemoglobin (not over 5%). The analytical methods were those of Folin and Wu (*C. A.* 13, 2541, 2545), Myers and Wardell (*C. A.* 12, 2592) and Coben and Smith (*C. A.* 13, 3201). I. G.

Origin and significance of the amyloid bodies "corpi amilacei" of the nervous system. CARLO GAMNA. Univ. Torino. *Arch. sci. med.* 44, 1–20(1921).—As studied in epidemic encephalitis these bodies stand in relation to the degenerative changes in the nervous tissue itself. M. HEIDELBERGER

Influence of the conditions of transfusion rate, pressure, and heterogeneous blood upon the subsequent maintenance of the arterial pressure. E. ZUNZ AND P. GOVAERTS. *Réunion soc. belge biol.* 1920, 144–6; *Physiol. Abstracts* 5, 403(1920); cf. *C. A.*, 14, 1145.—From 0.5 to 0.6 the apparent mass of its blood was removed from a dog. The blood pressure, after a rise, fell as mortal collapse became imminent. Then the citrated blood, previously removed from the dog, was injected. The blood pressure was completely restored to its original level. The secondary fall was exceptional and was always slight. However, if a dog was bled, and was then injected with blood obtained from another dog, the secondary decrease was usual; it varied in intensity according to the rate of transfusion and apparently was also influenced by the injected blood. This "heterogeneous" action could not have been due to isoagglutination of the erythrocytes, which is an exceptional phenomenon in dog blood; it was not due to hemolysis, as was shown by expts. JOSEPH S. HEPBURN

Studies on the brain stem. V. Carbon-dioxide excretion after destruction of the optic thalamus and the reflex functions of the thalamus in body temperature regulation. F. T. ROGERS AND S. D. WHEAT. Baylor Med. College. *Am. J. Physiol.* 57, 218–27(1921).—CO_2 production in pigeons, made poikilothermic by the destruction of the optic thalamus, varies directly with the body temp. variations. Such pigeons do not respond to atm. cold by increased heat production, nor to warmth by panting. "It is suggested that reflex changes of skeletal muscle tone and of the sympathetic system induced by stimulation of the temp. nerves of the skin involve the thalamus as an essential part of the functional pathway." J. F. LYMAN

Studies on the physiology of reproduction in birds. IX. The relation of stale sperm to fertility and sex in ring doves. O. RIDDLE AND ELLINOR H. BEHRE. Cold Spring Harbor, N. Y. *Am. J. Physiol.* 57, 223–49(1921).—Eggs laid by ring doves 8 days after sepn. from the male were, in some cases, fertile. This was the max. period during which sperm cells retained their fertilizing power. Staleness or over-ripeness of the sperm did not alter the sex ratio of the resulting young. **X. Inadequate egg shells and the early death of embryos in the egg.** O. RIDDLE. *Ibid* 250–63. Individual female pigeons which occasionally produce soft-shelled or thin-shelled eggs are not satisfactory for breeding purposes, since a high proportion of all the embryos in the eggs from these birds die in the shell. The second egg of a clutch is the more likely to have a thin shell, indicating a depletion of the animal's available supply of Ca. The early death of the embryos seems to indicate that something in the ovum (germ) is in disorder almost or quite simultaneously with the disordered functioning of the oviduct. Most of the aberrant shells and embryos were produced by females showing symptoms of rickets. **XI. Effects of feeding soluble calcium salts upon reproductive secretions and upon the total inorganic constituents of the egg shell.** O. RIDDLE AND M. C. E. HANKE. *Ibid* 264–74.—Feeding Ca lactate or Ca lactophosphate to female pigeons did not effect any change in the compn. or thickness of the egg shells produced. The eggs after Ca feeding were somewhat smaller than normal and contained a markedly diminished amt. of albumin. The production of thin- or soft-shelled eggs is probably not caused by an inadequate Ca supply in the food. **XII. The relation of nerve stimuli to oviducal secretions as indicated by effects of atropine**

and other alkaloids. O. RIDDLE AND C. V. KING. *Ibid* 275–90.—Atropine, cocaine, nicotine and pilocarpine had slight effects on the amts. and compn. of the egg albumin and egg shell secreted by pigeons. The occasional imperfect functionings of the avian oviduct which result in the production of inadequate egg shells probably cannot be even temporarily corrected by means of alkaloidal drugs. J. F. LYMAN

Respiration and circulation in the cat. II. The effect of hemorrhage and transfusion of gum-saline solution. Y. DOI. Physiol. Lab., Cambridge. *J. Physiol.* **55**, 249–52(1921); cf. *C. A.* **15**, 3293.—In cats under urethao anesthesia, fall of blood pressure after hemorrhage results in (1) an increased rate of breathing, (2) decreased vol. of a single respiration, (3) an increased total lung ventilation per min., (4) increased pulse, (5) decreased vol. of blood per heart beat, (6) decreased min. vol. of blood flowing through the lungs, (7) decreased vol. of O_2 absorbed hy the animal per min., (8) no marked change in % satn. of oxyhemoglobin of arterial blood and (9) a decrease in % satn. of oxyhemoglobin of venous blood. When the hlood pressure is lowered by hemorrhage, injection of Ringer soln. or gum-saline soln. raises it to normal and increases to normal the amt. of O_2 taken in by the animal and the min. vol. of blood flow through the lungs. Gum-saline soln. sustains these conditions for a longer time than does Ringer fluid. J. F. LYMAN

Variation in the content of zinc in the organism of the rabbit during growth. GABRIEL BERTRAND AND R. VLADESCO. *Compt. rend.* **173**, 54–5(1921); cf. *C. A.* **15**, 1922.—Twelve rabbits from two does of the same race, all of which were grown under special surveillance and received the same rations, were examd. for Zn at periods of growth ranging from a few hrs. to 6 weeks. The wts. of the animals ranged from 32.1 to 1195 g. Animals from a few hrs. to 2 days old averaged 81.2% H_2O, from 5 to 20 days 72.4, and from 20 days to 6 weeks 71.0. The Zn content was at a max. during the first 24 hrs. of life, when there were present 12.3 mg. per 100 g. of dry matter. During lactation the Zn content diminished to 4.7 mg. per 100 g. at 25 days, but after weaning the Zn content rapidly increased reaching 15.2 mg. at 6 weeks. (Cf. following abstract.) Also in *Bull. soc. chim.* **29**, 915–7(1921). L. W. RIGGS

Probable intervention of zinc in the phenomena of fecundation in vertebrate animals. G. BERTRAND AND R. VLAOESCO. *Compt. rend.* **173**, 176–9(1921).—In a preceding paper (cf. *C. A.* **15**, 1922) it was noted that the mammary glands and testicles of the horse were particularly rich in Zn although the conteot of the metal in these organs was not const. Observations upon herring during a period of sexual activity, the month of March, showed that the testicles cootained more than twice as much Zn per 100 g. of dry matter as the rest of the body. At the eod of the active season in May the testicles contained less than ooe-half as much Zo per 100 g. of dry matter as the muscles and skeleton. In the female herring there was practically no difference in the Zn content of the ovaries and of the remainder of the body during the month of March. The results of 18 detns. of Zn in the genital organs of man, pig, sheep, bull and gray rat showed the prostate and also the seminal vesicles to contain more Zn than the testicles. The Zn in the epididymis was more in 2 cases and less in 2 than in the testicles of the same animal. The seminal fluid in the horse and in 3 men contained 48.6, 57.2, 155.2 and 202.0 mg. of Zn per 100 g. of dry matter, resp. These findings support the statement that Zn plays an important role in the function of reproduction in vertebrate animals. L. W. RIGGS

Localization of glycogen in the liver and muscles of dogs fed with a view to the maximum production of that reserve. MME. Z. GRUZEWSKA AND FAURÉ-FRÉMIET. *Compt. rend.* **173**, 254–7(1921).—After a fast of 8 or 9 days the dogs were fed a ration consisting of 100 to 150 g. of horse meat, according to the wt. of the dog, and as much rice and sugar for several days. The liver and muscles were then examd. chemically and

histologically. A young dog gave the most striking results, there being 22.3 g. of glycogen per 100 g. of fresh liver. The hepatic cells were greatly distended, the liver was much enlarged, and a diminution in the wt. of albumoids per 100 g. of fresh liver was observed. With an old dog the increase in the size of the liver and the increase of glycogen were much less, while the percentage of albumoids remained high. The amt. of glycogen in muscles and in the heart bore no relation to the increased glycogen in the liver. L. W. RIGGS

Liver as a blood-concentrating organ. PAUL D. LAMSON AND JOHN ROCA. Johns Hopkins Univ. *J. Pharmacol.* **17**, 481–97(1921).—The disappearance of intravenously injected isotonic salt soln. from the blood is due, in large part, to the action of the liver. The rate of disappearance is decreased 4 times or more by the removal of the liver. The addition of epinephrine to the injected fluid greatly increases its rate of disappearance in the normal animal but has no effect in an animal whose liver has been removed from the circulation. The theory that any increase in arterial pressure will cause a general filtration into the tissues is incorrect. The addition of epinephrine to intravenous salt infusion for the purpose of raising the blood pressure should be discouraged as it accelerates fluid loss. The acute polycythemia found in emotional disturbances, asphyxia, exercise, and after the injection of certain drugs can all be explained by obstruction of the hepatic blood flow by constriction of the hepatic veins, but as yet it is not proved that they occur in this manner only. Fluid may be lost from the body by any of the channels of excretion. It may leave the blood stream by diffusion in certain pathol. conditions, but this mechanism in the liver is the only known mechanical device by which fluid may be removed from the circulation by filtration and yet not be lost from the body. C. J. WEST

G—PATHOLOGY

H. GIDEON WELLS

Serology of the spinal fluid and blood in epidemic encephalitis. W. M. KRAUS AND I. H. PARDEE. New York. *Arch. Neurol. Psychiatry* **5**, 710–22(1921).—A study of 245 cases shows increase of mononuclear cells, globulin, sugar (a few cases only examd.), usually increased pressure, and positive colloidal Au test. Blood showed normal values for red corpuscles and hemoglobin, variable leucocyte content and normal sugar. It is suggested that the thin membrane of cells sepg. the blood from the perivascular spaces may, by being injured, permit the amt. of sugar in the spinal fluid to approach that in the blood. A. T. CAMERON

Epidemic encephalitis. M. E. ALEXANDER. Waterbury. *Arch. Neurol. Psychiatry* **6**, 44–60(1921).—A study of 25 cases. Chem. examn. of blood revealed nothing unusual. Five cases showed slight albuminuria. Nine cases showed glucosuria (0.1 to 1.5%). It was not present throughout the 24 hrs. and could not be related to time of day or meals. The spinal fluid showed in all cases a trace of globulin, in 10 a marked amt. Reducing sugar was present in normal amt. except in 3 cases (diminished). A. T. CAMERON

Epidemic encephalitis (Lethargic encephalitis). L. B. HOHMAN. Johns Hopkins Hospital. *Arch. Neurol. Psychiatry* **6**, 295–333(1921).—Study of 23 cases, of which 19 showed in the spinal fluid cell increase of small mononuclear type, increase in globulin, no distinctive type of colloidal Au curve, and in blood, slight leucocytosis. A. T. C.

Comparative study of the sugar content of the spinal fluid in diseases of the nervous system. L. D. STEVENSON. St. Louis. *Arch. Neurol. Psychiatry* **6**, 292–4 (1921).—Benedict's method led to distinctly higher results than those given by Shaffer's method. Four cases of encephalitis gave an av. of 60 mg. sugar per 100 cc. by Shaffer's method. Former values with Folin's method were much higher. It is suggested

that some other reducing substance may be present in cases of encephalitis, which may not interfere with the Shaffer method. A. T. CAMERON

Comparative results of colloidal mastic and colloidal gold tests. A. KRIDEL AND J. E. MOORE. Baltimore. *Arch. Neurol. Psychiatry* **6**, 163–73(1921).—Results show fairly close parallelism. When there is disagreement, the mastic test detects abnormalities more frequently. It is, therefore, recommended. A. T. CAMERON

Auto-hemagglutination. C. J. BOND. *Brit. Med. J.* **1920**, II, 925–7, 973–6.—All red blood corpuscles can form hemagglutinogen under certain conditions. This, like agglutinin, exists in a non-sp. form, and in a graded series of sp. forms, allied but not identical in compn. or character. So far it has only been found in combination with or attached to the surface or stroma of red cells, and does not appear to exist in serum in the free state. Sp. and non-sp. agglutinins are present in serum in the free state; both kinds are removed by filtration through porcelain. A. T. CAMERON

Intermittent albuminuria in children. F. MOOR. *Brit. Med. J.* **1921**, I, 671–2.—The condition is common, and is not a form of kidney disease. It is probably a symptom of several diseases. A. T. CAMERON

A resumé of diabetes mellitus. R. W. MANN. Toronto. *Can. Med. Assoc. J.* **11**, 243–51(1921).—Chem. and clinical data of 5 cases are included. A. T. CAMERON

Prognostic value of the study of the blood creatinine in nephritis. I. M. RABINOWITCH. Montreal. *Can. Med. Assoc. J.* **11**, 320–2(1921).—A study of 14 cases with complete post-mortem examn. yields additional support to the statement that figures of over 5 mg. per 100 cc. indicate an early termination. Comparison of a series of such high figures, however, does not disclose any definite relation between amt. and duration of disease. A. T. CAMERON

Acidosis in nephritis. E. H. MASON. Montreal. *Can. Med. Assoc. J.* **11**, 424–6 (1921).—Details of chem. analysis of blood and urine in a case. A. T. CAMERON

Fragilitas ossium. C. W. BURNS. Winnipeg. *Can. Med. Assoc. J.* **11**, 522–3 (1921).—Report of a case. Ca excretion (urine) was above normal. A. T. CAMERON

Simple method of determining the approximate degree of acidosis in diabetes mellitus. I. M. RABINOWITCH. Montreal. *Can. Med. Assoc. J.* **11**, 526–8(1921).—Details of 5 cases in which the Van Slyke and Palmer procedure (*C. A.* **14**, 1689) was used. A. T. CAMERON

Glucosuria of malarial origin. A. CASTELLANI AND J. G. WILLMORE. *Brit. Med. J.* **1921**, II, 286.—Reports of 2 cases which show that the condition may become so severe as to simulate true diabetes mellitus. Quinine administration cured the glucosuria without any dietetic treatment. A. T. CAMERON

The chemical composition of saliva in a case of sialorrhea. R. CLOGNE AND A. RICHAUD. *Bull. soc. chim. biol.* **3**, 69–70(1921).—The compn. showed little alteration. A. T. CAMERON

Blood analyses in cases of catatonic dementia precox. S. UYEMATSU AND T. SODA. *J. Nervous Mental Diseases* **53**, 367–75(1921).—There is no definite and abs. blood formula for the catatonic dementia precox group. In 24 of 32 cases studied uric acid was decreased in 15 blood sugar was increased. The av. deviation of each constituent examd. (urea, uric acid, sugar, creatine, creatinine, non-protein N) was higher than normal; this suggests an unstable metabolism. A. T. CAMERON

Adolescent tetany and its relation to guanidine. F. J. NATTRASS AND J. S. SHARPE. Glasgow. *Brit. Med. J.* **1921**, II, 238–9.—Administration of parathyroid, thyroid, or salol to a girl aged 17 had no definite beneficial effect. Guanidine was excreted chiefly as methylguanidine (6.7 mg. per kg. per day). There was no excess of ethereal sulfates in the urine and no evidence of pancreatic deficiency. A. T. CAMERON

Value of laboratory reports on stools in cases of suspected amebic dysentery,

and their interpretation by the clinician; with a special note on the diagnostic value of Charcot-Leyden crystals. J. G. THOMSON AND A. ROBERTSON. *Proc. Roy. Soc. Med.* **14**, Sect. Tropical Dis. and Parasitol., 33–44(1921).—Charcot-Leyden crystals are probably the result of cytolytic action of *Entamoeba histolytica* on the body cells. They are present in a very high percentage of cases of amebic dysentery, more commonly when the disease is of long standing. Their presence is diagnostic of *Entamoeba histolytica*. A. T. CAMERON

Blood sugar studies in dementia precox and manic-depressive insanity. T. RAPHAEL AND J. P. PARSONS. Ann Arbor. *Arch. Neurol. Psychiatry* **5**, 687–709(1921).—Tolerance curves differing from normal and among themselves were obtained in hypomanic and depressed phases of manic-depressive insanity and in dementia precox. In each group common features suggested a type curve. Many had a prolonged max. level much above normal, yet glucosuria was seldom present. The curve for dementia precox varied with the clinical phase. A. T. CAMERON

Toxic agents developed in the course of acute intestinal obstruction, and their action. H. B. STONE. Baltimore. *Surg. Gynecology Obstetrics* **32**, 415–9(1921).—A review. A. T. C.

Bone atrophy. N. ALLISON AND B. BROOKS. St. Louis. *Surg. Gynecology and Obstetrics* **33**, 250–60(1921).—Expts. on dogs show nonuse has no effect on chem. compn. of bone matrix. An entire bone may lose more than 25% of its mineral constituents in 24 days of nonuse. This is due to loss of bone matrix, not to change in its compn. A. T. CAMERON

Discussion of renal efficiency tests. H. MACLEAN, F. C. BOYD, *et al.* *Brit. Med. J.* 1921, II, 425–31. A. T. C.

The excretion of methylene blue in tuberculosis. ROBERT PFEIFFER. Vienna. *Beitr. Klin. Tuberkulose* **47**, 46–53(1921).—By Müller's classification of methylene blue (*Arch. klin. Med.* **63**, 130) into 8 leuco products, it was found after the *per os* administration of 2–5 mg. of methylene blue and the hourly examn. of the urine that tuberculous patients possess an exceptional power to destroy methylene blue; within 6 to 10 hrs. no M_α, or L_β or L_γ was excreted. Cases of influenza and some cases of chronic nephritis especially with polyuria also showed a lessened excretion, the reason in the latter case being probably not identical with that in tuberculosis. The fermentative destruction of methylene blue in dilns. of 1 : 5,000 to 1 : 100,000 by various tissues, lung, liver, spleen, kidney, muscle, lymph glands and brains was studied. Lung tissue possessed the greatest ability to destroy the dye. Certain inconsistencies existed, however, in that blood also destroyed it. The blood from cases of tuberculosis changed the dye more rapidly than other bloods, while the serums did not differ in this respect, being inactive. Heating the ground organs did not destroy this action, and extn. of the tissues with ether enhanced it. Tissues from various diseased individuals did not act differently from normal tissues. Tuberculous lung tissue, however, instantly changed the dye from blue to a green-yellow or green-blue color, doing so much more rapidly than normal lung tissue. H. J. CORPER

Reflections of a physician apropos of the Wassermann reaction. E. COMBE. *J. Pharm. Belg.* **3**, 637–9(1921).—A descriptive article dealing with the role played by the antigen, antibody and complement in the fixation process. A. G. DUMEZ

Some characters of the cleavage products of certain bacteria, with special reference to their toxicity and antigenic properties. S. R. DOUGLAS. *Brit. J. Exptl. Pathol.* **2**, 175–191(1921).—Emulsions of acetone-extd. bacteria which have been digested with trypsin for a suitable period have a toxicity which is the same as, or at times greater than, that of emulsions of untreated bacteria of equal density. The toxin present in the tryptic digests is the specific bacterial endotoxin which is usually produced in the

body by the lytic action of the body fluids. Antitoxin prepd. by the injection of untreated bacteria completely neutralizes the toxic properties of the tryptic digests. When bacterial digests are injected into animals the bactericidal and pptg. powers are greatly increased. Antitoxin also is formed but there is no increase of either the agglutinating or opsonic powers. This shows that the agglutinating and pptg. properties of the serum, instead of being very closely related or even identical, are quite distinct from one another. It is also suggested that the antigens giving rise to the agglutinating and opsonic powers are produced during the very early stages of the soln. of the bacteria by the body fluids, while the antigens, in response to which the body produces the bactericidal, antitoxic and pptg. powers, are formed during a comparatively late period of the lytic process. Repeated injections of untreated bacteria cause diminution of the lytic power of the blood fluids even when comparatively small doses are employed. This would account for the difficulty in producing potent anti-endotoxic sera, as the loss of the lytic power would prevent the injected bacteria being digested *in vivo* as far as the toxic phase, and, in consequence, no antitoxic response would be evoked. Digestion of the bacteria *in vitro* presents the endotoxin preformed to the body, and so may lead to the production of much more potent antitoxic sera. Digests of bacteria should prove to be more suitable for testing the potency of anti-endotoxic sera than emulsions of untreated bacteria, and since such digests contain large amts. of the specific precipitable substance they should be employed in estg. the pptg. properties of sera. Other tests in which such digests may be employed are: (1) As antigens in complement-fixation tests; here it is suggested that the activity of a disease might be recognized by the detection in the blood of antibodies to particular products of bacterial cleavage by using as the antigen the corresponding phase of a tryptic digest. (2) As vaccines for therapeutic use, especially in those cases which have become tolerant to the ordinary vaccine, a condition in which the body appears to have lost all power of breaking down the bacteria of the vaccine. HARRIET F. HOLMES

The occurrence of hemolytic substances in normal urine. E. PONDER. *Brit. J. Exptl. Path.* **2**, 192–3(1921).—Sixty-four % of normal unselected urines were found to be hemolytic. If the non-hemolytic specimens had been examd. repeatedly they would probably have been found to be hemolytic at some time. Since the % of positives obtained by the examn. of 200 normals is distinctively less than the % obtained from 300 cases of insanity (*C. A.* **15**, 1927) it seems probable that there is a greater tendency to the excretion of hemolytic substances in the urine among the insane, and doubtless also in many other pathological conditions, than there is in the normal individual. On the other hand the occurrence of hemolytic substances in itself is not abnormal. HARRIET F. HOLMES

Metabolism in vascular hypertonia. K. HITZENBERGER AND M. RICHTER-QUITTNER. Vienna. *Wien. Arch. inn. Med.* **2**, 189–216(1921).—The carbohydrate and purine metabolism is studied in 38 cases of high blood pressure. Hyperglucemia occurs as a rule with both primary and secondary vascular hypertonia. The hyperglucemia in hypertonia differs from that in diabetes, in that it is independent of the diet. It does not result from a disturbance in assimilation of sugar but in continued overproduction of sugar. When diabetes and vascular hypertonia occur in combination, the hyperglucemia is greater than is indicated by the sugar excretion. In vascular hypertonia there is frequently an excess of uric acid in the blood. This hyperuricemia is not due to a retention of uric acid, thus differing from the hyperuricemia of gout. Administration of food rich in purines is followed by an increase in uric-acid excretion, which is not the case in gout. The syndrome, hypertonia, hyperglucemia, and hyperuricemia, seems to be the expression of a disturbance of metabolism, perhaps an increased functioning of the adrenal. HARRIET F. HOLMES

Pathology of gastric secretion. M. Leist and O. Weltmann. Vienna. *Wien. Arch. inn. Med.* 2, 245–70(1921).—Suhacidity and anacidity of the gastric secretion occur frequently in various forms of dropsy. It is not improbable that this subacidity or anacidity may be due to the retention of Cl in the tissues and the unavailability of Cl for the gastric secretion. Harriet F. Holmes

Blood picture and blood platelets under the influence of calcium injected intravenously. Otto A. Rösler. Univ. Clinic of Graz. *Wien. Arch. inn. Med.* 2, 281–92 (1921).—0.1 g. Ca lactate in 10 cc. physiol. NaCl soln. was injected intravenously in a number of healthy persons and patients suffering from tuberculosis, malaria and other diseases. There was a 6–18% increase in the polymorphonuclear neutrophile leucocytes at the expense of the lymphocytes, lasting for several hrs. There was either no increase or only a slight increase in the total number of leucocytes. The number of blood platelets fell to a half, and in some cases to a third of the original count. Morphological changes were noted, such as anisocytosis and pale staining plasma. There was a shortening of the coagulation time of the blood, which ran parallel to the reduction in the number of blood platelets. Harriet F. Holmes

Bacteriolytic substances in leucocytes and their relation with alexin. I. Gengou. Pasteur Inst. Brussels. *Ann. inst. Pasteur* 35, 497–512(1921); see *C. A.* 15, 894. E. R. Long

The thermolability of complement, in relation to the hydrogen-ion concentration. Calvin B. Coulter. Hoagland Lab., Brooklyn, N. Y. *J. Gen. Physiol.* 3, 771–82 (1921).—Complement when dild. in distd. water undergoes the least heat destruction at p_H 6.1–6.4. The inactivation is closely related to the properties of the euglobulin fraction of the serum, destruction being least at the reaction at which the euglobulin is least sol. The reaction involved probably represents the isoelec. point of a compd. of the euglobulin with some other substance in the serum. It is chiefly or entirely the ions of the euglobulin compd. which react; they combine or interact with substances in the pseudoglobulin and albumin fraction. The behavior of the euglobulin depends upon its condition of ionization: On the acid side of p_H 6.1–6.4, destruction by heat increases with increasing acidity whether or not NaCl is present; on the alk. side of this point, NaCl protects complement from heat destruction because of the depression in the ionization of the euglobulin. Cf. *C. A.* 15, 1032. Chas. H. Richardson

H—PHARMACOLOGY

ALFRED N. RICHARDS

The study of local anesthetics. III. Hydroxyamino acids. Ernest Fourneau. Pasteur Institute. *Bull. soc. chim.* 29, 413–6(1921).—The benzoyl derivs. of $Me_2NCH_2CMe(OH)CO_2H$ are less toxic than the benzoyl derivs. of the corresponding alc. The salts, however, are decidedly acid to indicators and their solns. are much too irritating to be used in local anesthesia. F., believing that the introduction of a new aminated group into the mol. would give neutral salts, prepd. the benzoyl deriv. of *β,β-bis(dimethylamino)-α-hydroxyisobutyric acid*, $(Me_2NCH_2)_2C(OH)CO_2H$. He found, however, that the hydrochloride of this compd. was not neutral and that subcutaneous injections of a 1% soln. of it were irritating. It is, therefore, not superior to products already in use. F., starting with dichloroacetone, describes the synthesis of the *hydrochloride* of *ethyl α-benzoyloxy-β,β-bis(dimethylamino)isobutyrate*. J. A. B.

Some of the effects of chronic lead poisoning, with special reference to arteriosclerosis. G. B. Page. *J. State Med.* 29, 161–8(1921).—Many minor ills among work people are due to plumbism. Arterial disease is considered one of the possible results of lead poisoning and saturnine nephritis has been allowed as a basis for compensation

claims at law. The author observed the frequent occurrence of arteriosclerosis among workers in lead at British naval depots and noted that old workers, while seldom ill, are never really well. The mechanism of the causation of arteriosclerosis, hyperplesis and renal disease by lead poisoning is discussed. Lead has a deleterious effect on the musculature of the blood vessels, but injury to the renal epithelium is the first step. The damaged cells then fail to excrete toxic products, and high blood pressure and arteriosclerosis results. The susceptibility to plumbism varies. Cleanliness is prescribed as the most effective preventive. JAMES A. BRADLEY

The relation between chemical constitution and physiologic action. AD. OSWALD. Zurich. *Schweiz. Chem. Ztg.* 1921, 299–303, 325–9, 337–41.—This is a comprehensive review. H. C. HAMILTON

Some observations of the hemolytic action of certain quinine salts on the erythrocytes of different individuals and on the resistance of newly formed corpuscles to hemolysis under the influence of distilled water. U. N. BRAHMACHARI AND PARIMEL SEN. Campbell Medical School, Calcutta. *Biochem. J.* 15, 463–5(1921).—Quinine dihydrochloride is more hemolytic than either the hydrochloride, the disulfate or the sulfate. Acid salts are more hemolytic than the corresponding neutral salts. Free HCl or free H_2SO_4 is more hemolytic than a soln. of quinine dihydrochloride or quinine disulfate contg. the same amt. of HCl or H_2SO_4, resp. Resistant corpuscles were increased after repeated bleeding. Erythrocytes of different individuals vary differently in their resistance to hemolysis under the influence of a quinine salt. B. H.

Relation of homeopathic remedies to modern diagnostic tests. ALBERT E. HINSDALE AND R. W. HOFFMAN. Ohio State Univ. *J. Am. Inst. Homeopathy* 14, 215–31 (1921).—Administration of $HgCl_2$, As_2O_3, P, $K_2Cr_2O_7$, terebinthine, apis, and cantharides to rabbits decreased the power of the kidney as an excretory organ as measured quantitatively by the *phenolsulfonephthalein renal function test.* Intramuscular injection of these remedies into rabbits produced a marked condition of acidosis, as measured by detn. of the *CO_2 combining power* of the blood plasma in the Van Slyke app. The *urea* content of the blood was influenced but little by cantharides, was moderately increased by apis, was increased to approx. twice its normal value by As_2O_3, and was increased to more than 13 times its normal value by $HgCl_2$. The *total solids* in the blood were decreased by $HgCl_2$, by As_2O_3 to approx. half the normal value, by P to approx. $^3/_4$ the normal value and by U. S. P. tincture of Fe to approx. $^2/_3$ the normal value. The *blood sugar* was always increased by $UO_2(NO_3)_2$. With syzygium, the predominating early effect was an increase, the predominating late effect a decrease in the blood sugar. The exptl. animals usually decreased in body wt. In normal rabbits, the av. CO_2 combining power of the blood plasma was 46.2. JOSEPH S. HEPBURN

Action of the karaka nut. A. E. HINSDALE. Ohio State Univ. *J. Am. Inst. Homeopathy* 14, 246(1921).—Injection of the tincture of the karaka nut into the lymph sac of frogs produced paralysis, central in origin. JOSEPH S. HEPBURN

I—ZOÖLOGY

R. K. GORTNER

Direct demonstration of the existence of a metabolic gradient in annelids. LIBBIE H. HYMAN AND ALBERT E. GALIGHER. Univ. Chicago. *J. Exptl. Zoöl.* 34, 1–16 (1921).—The polychetes *Nereis virens* and *N. vexillosa* and the oligochete *Lumbricus inconstans* were cut into pieces and the O_2 consumption per unit wt. of pieces from the anterior, middle and posterior regions of the body was detd. It was found that the posterior end consumes the most, the anterior less and the middle region the least O_2 per unit wt. in a given time. These results confirm the conclusions drawn from other methods in showing a definite metabolic gradient in these forms. C. H. R.

The toxicity of acids to infusoria. II. The role of molecule and of ions. M. E. COLLETT. Clark Univ. and Buffalo Med. Dept. *J. Exptl. Zoöl.* **34**, 67–74(1921); cf. *C. A.* **14**, 3478.—The toxicity of a number of org. acids to *Paramecium* and *Euplotes* was studied. The following acids were used alone or with HCl or their Na salts: Formic, acetic, propionic, butyric, valeric, caproic, benzoic, salicylic, lactic, tartaric, succinic, and citric. Depression of the ionization of these acids with HCl does not, on the first addition, affect the toxicity, but with further addition, toxicity is increased. This may be due to the disappearance of the toxic org. anion (when a small amt. of HCl is added) or to the partial antagonism of the mol. by HCl. Only salicylic, benzoic, and citric acids have anions which are toxic at 0.01 *M* or less. The relative toxicity of the Na salts at 0.01 *M* concn. is as follows: (*Paramecium*) salicylate > benzoate > tartrate = succinate > citrate > formate = valerate = chloride = lactate; for *Euplotes* citrate > salicylate > benzoate = tartrate > succinate > formate = valerate = lactate. Mixts. of certain acids (formic, acetic, butyric, valeric) with non-toxic concns. of their salts were more toxic than could be accounted for by the p_H of the mixts. Benzoic, salicylic and citric acids (the latter with *Euplotes* only) when mixed with dil. solns. of their Na salts were more toxic than their p_H or the toxicity of the salts alone would indicate. It is believed that the mols. of such acids are themselves toxic. Lactic, succinic and tartaric acids were not toxic at the concns. used. **III. Antagonism of the toxic action of acids by inorganic chlorides.** *Ibid* 75–99.—*Paramecium* and *Euplotes* were used as test animals. The acids can be divided into two groups on the basis of the effect produced. The first group includes HCl, formic, acetic, succinic, lactic, tartaric, citric; the second group, butyric, caproic, benzoic, salicylic, phenylacetic, the latter contg. the more lipoid-sol. members. NaCl diminishes the toxicity of all acids to *Paramecium*. For *Euplotes*, it is efficient with the acids of the second group between 0.01–0.1 *M*, but only with lower concns. (0.01–0.05 *M*) of acids of the first group. The relative antagonistic power of the alk. earth chlorides is as follows: (*Paramecium*) Ca>Sr>Ba>Mg, for acids of group 1; Ca>Sr>Ba>Mg, for acids of group 2; (*Euplotes*) Ca>Ba>Sr>Mg group 1; Ca>Sr>Ba>Mg group 2. The addition of NaCl in the ratio of 10 to 1 mol. to the alk. earth chlorides increases their antitoxic power toward acids of both groups, with exceptions as follows: 0.01 *M* $CaCl_2$ and $SrCl_2$ have their antagonistic power diminished by acids of the 1st group and are left unchanged by acids of the 2nd group (*Paramecium*); the power of 0.005 and 0.1 *M* $SrCl_2$ is greatly diminished by acids of the 1st group (*Euplotes*). Heavy metal chlorides show antagonistic power in the following order: (*Paramecium*) Mg>Co>Mn>Cd>=Ni=Zn, 1st group; Mg>Mn>Co>Cd>Ni=Zn, 2nd group. (*Euplotes*) Mg>Mn>Co>Cd>Ni=Zn, 1st group; Mg>Mn>Cd>Co>Ni=Zn, 2nd group. Antagonistic power is limited to some extent by the toxicity of the salts. The toxicity of the pure salts (0.01 *M*) is: (*Paramecium*) Ca<Sr<Mn<Ba<Mg<Co<Cd<Ni=Zn; (*Euplotes*) Ca<Sr<Mn<Mg<Ba<Co<Cd<Ni<Zn. When combined with NaCl a reduction in toxicity occurs with all salts except Sr, Cd, and Co (*Euplotes*). The visible changes in the protoplasm due to the acids are described. Efficiently balanced solns. of salt and acid delay changes in the protoplasm as if the acid were unable to penetrate the surface. The swelling which eventually appears in most of the mixts. is probably due to the small amt. of acid which is able to penetrate in spite of the salt protection. There is a discussion of the literature followed by a bibliography of 42 titles. "The facts observed in the antagonism of the acids by salts are consistent with Clowes' tentative identification of the surface lipoid as a soap, for the Na soap would protect against lipoid-sol. substances and the Ca soap against water-sol. substances. There may also be Na or Ca protein salts of unlike soly., resembling the Na and Ca gelatin salts which Loeb (*J. Biol. Chem.* 29, viii) has found to differ widely in hydration. My expts., how-

ever, taken by themselves, are insufficient to establish the exact nature of the surface film or to explain the specific differences observed." CHARLES H. RICHARDSON

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Nutrients and foods. J. GROSSFELD. *Chem. Ztg.* **45**, 753-4(1921).—A generalization of the latest findings relating to nutritive value and accessory factors of foods. H. A. LEPPER

Report of committee to coöperate with other committees on food definitions. WILLIAM FREAR, JULIUS HORTVET AND C. D. HOWARD. *J. Assoc. Official Agr. Chem.* **4**, 586-94(1921).—Subjects discussed are cheese and butter. A standard for cheeses is proposed. No change is recommended in the present standard for butter as given in *U. S. Dept. Agr. Circ. Office of Secretary*, No. 136. H. A. LEPPER

Opinions on food control. K. BRAUER. Cassel. *Chem. Ztg.* **45**, 783(1921).—The opinion of B. on this subject (cf. Behre, *C. A.* **15**, 275, 3338; Forster, *Z. offentl. Chem.* **26**, 5, 241). H. A. LEPPER

Report on meat and meat products. RALPH HOAGLAND. U. S. Bur. of Animal Ind. *J. Assoc. Official Agr. Chem.* **4**, 490-502(1921).—Collaborative work on the phosphotungstic acid method for dextrose in meat is considered fairly satisfactory, especially in detn. of small quantities of sugar. The method is considered superior to any other method known to H. and is recommended for tentative adoption. Comparison of drying in air at 100° and in a vacuum desiccator over H_2SO_4 was made for H_2O in meat. Slightly greater loss is obtained by the former method but the latter is preferred where high degree of accuracy is desired and residue is to be used for fat extn. H. A. LEPPER

Report on the separation of nitrogenous compounds in meat products. L. C. MITCHELL. *J. Assoc. Official Agr. Chem.* **4**, 502-6(1921).—Collaborative study of the Schlösing-Wagner method for the detn. of nitrates in meat was made on beef ext. Further work is recommended and modifications are suggested. H. A. LEPPER

Methods of freezing fish. I. FOOD INVESTIGATION BOARD OF H. M. DEPT. SCI. AND IND. RESEARCH. *S. African J. Industries* **4**, 629-37(1921).—A discussion of the handling of large quantities of common fish such as herring or spats during a glut, so that they may be held in storage until the market is capable of absorbing them, or to keep a canning factory in steady employment. Freezing in brine cooled to −12.2° for one hour is recommended as the best method for herring. The ice block method is not so economical and the glazing process is not as applicable to handling gluts as the brine method. Packing the fish in boxes, stacking boxes to allow least possible air space, and maintaining as constant temp. as possible are recommended for cold storage of frozen fish to preserve flavor and color and prevent bacterial growth. The brine method checks the multiplication of bacteria and partially sterilizes the surface of the fish. Thawing may be carried out in air or H_2O. H. A. LEPPER

Report on eggs and egg products. C. E. MARSH. Boston. *J. Assoc. Official Agr. Chem.* **4**, 507-16(1921).—The Folin (*C. A.* **7**, 1208) and the Hendrickson and Swan (*C. A.* **12**, 2029) methods for ammoniacal N and the so-called U. S. Dept. Agr. and the Klein modification of Benedict Lewis methods for dextrose in eggs were compared by collaborative study. The methods are given. The Folin method is recommended for tentative adoption for ammoniacal N in eggs. Further study of the dextrose methods is recommended. M. found the Klein method quicker and results by it more uniform. The general opinion about tests for detn. of decompn. of dried eggs is that none is satisfactory. The Juckenack method for lecithin P_2O_5 in dried egg was compared with

a method which shortens the period of extn. from 10 to 2 hrs.; the results were practically the same. H. A. LEPPER

Discussion of report of referee on egg products. H. W. REDFIELD. U. S. Food and Drug Inspection Sta., N. Y. *J. Assoc. Official Agr. Chem.* 4, 516–20(1921).—The report of Marsh (preceding abstract) is criticized on the basis of an exhaustive investigation reported in U. S. Dept. Agr., *Bull.* 346 (*C. A.* 14, 2518). H. A. LEPPER

Sugar content of the hen's egg. J. S. HEPBURN AND E. Q. ST. JOHN. Hahnemann Med. Coll., Phila. and Philadelphia Clinical Lab. *J. Am. Inst. Homeopathy* 14, 339–43(1921).—The method of Folin and Wu for the detn. of the dextrose content of blood (*C. A.* 13, 2541; 14, 2353) has been adapted to the detn. of the dextrose content of eggs. In individual *fresh* eggs analyzed within 36 hrs. of laying, the following minimum, max., and av. percents of dextrose were obtained; each set of figures is based on 6 samples. Whole egg 0.36 to 0.49, av. 0.45%; white free from yolk 0.29 to 0.57, av. 0.47%, yolk free from white 0.11 to 0.15, av. 0.14%, yolk commercially sepd. 0.16 to 0.35, av. 0.25%. In eggs, which had been preserved in *water glass* for 9 months, the dextrose content of the whole egg, of the white free from the yolk, and of the commercially separated yolk lay practically within the limits found for fresh eggs. The dextrose content of *frozen whites*, which had been in cold storage for an unknown period of time, was well within the values found for fresh whites. A sample of *putrid white* contained no dextrose. JOSEPH S. HEPBURN

Chemical studies of cranberries during storage. F. W. MORSE AND C. P. JONES. Mass. Agr. Expt. Sta., *Bull.* 198, 75–87(1920); see *C. A.* 14, 3730. W. H. ROSS

Chemical analysis of prunes, dried apricots and almonds. ANON. California Expt. St., *Ann. Rept.* 1919, 35–8.—Prunes contain approx. 50% sugar and 20–30% H_2O. Dried apricots contain 11.5–38% H_2O and 40–56% sugar. Almonds contain over 50% fat, 20–26% protein, 3–3.50% ash, and 4–10% H_2O. Domestic almonds are equal in nutritive value to the imported article. WILLIAM HAZEN

A chemical characteristic of cassava and rice flours. LOUIS DESVERGNES. *Ann. chim. anal. chim. appl.* 3, 205–6(1921).—Wheat bran is often adulterated with cassava flour to produce whiteness. The differences in protein and ash will not permit detection of 20% cassava by chem. means. A color test is proposed to detect cassava. Add to 10 g. of sample 45 cc. alc. and 5 cc. HCl (22%) in a 200-cc. flask, boil 5 min. under reflux. Filter after cooling. Pink colored filtrate indicates cassava or rice. If a yellowish brown color due to bran masks the pink, add 50% of C_6H_6 and 25% H_2O. The sepd. C_6H_6 will be colored brown and dil. alc. layer underneath pink. With this test oats give a straw-yellow, wheat light rose yellow, yellow corn light yellow, cassava cerise-red, barley light straw-yellow, rice deep rose, and rye a yellowish rose coloration. H. A. LEPPER

Report on baking powder. H. E. PATTEN. *J. Assoc. Official Agr. Chem.* 4, 538–9(1921).—The Corper-Bryan method for Pb in baking powders gave excellent results with experienced operators. The thin paste resulting from the acidification and hydrolysis must not be too acid and need not be clear. In the Chittick method for Pb, filtration may be hastened by filter cones and MeOH can be used for washing. The Wagner-Ross method for F (*C. A.* 12, 29) was recommended for adoption as collaborative results were very good. The baking powder must be ignited or leavened and ashed to insure perfect dryness for successful results (cf. *C. A.* 15, 904). H. A. LEPPER

Shortening—its definition and measurement. CLARK E. DAVIS. *J. Ind. Eng. Chem.* 13, 797–9(1921).—"That cake which requires the least load to measure its breaking strength is the shortest, that which requires the heaviest load is the least short. The best shortening is that material which when baked in a dough gives to the product a min. breaking and crushing strength." Of 14 fats and oils studied lard was the best

shortening agent. Partial hydrogenation of an oil increases its shortening power. An app. is described and illustrated by drawings for measuring shortening value and a method for classifying *flour* is suggested. H. A. LEPPER

Report on vinegar (Determination of glycerol in cider vinegar). W. A. BENDER AND V. B. BONNEY. *J. Assoc. Official Agr. Chem.* **4**, 468–8(1921).—Attempt was made to combine into one operation the 90% alc., and abs. alc. and Et_2O extn., with the subsequent evapn., and transfers in the detn. of glycerol in vinegar. None of the 5 procedures tried was satisfactory. H. A. LEPPER

Report on flavoring extracts. A. E. PAUL. U. S. Food and Drug Inspection Sta. Chicago. *J. Assoc. Official Agr. Chem.* **4**, 468-79(1921).—Wichmann and Dean's qual. method for coumarin (*C. A.* **12**, 1669), Folin's colorimetric method for vanillin (*C. A.* **7**, 1769) and Wichmann's modified Pb no. (*C. A.* **15**, 2518) in vanilla ext. were found to be meritorious, but sufficient data have not been collected on authentic samples to make their use satisfactory for interpretation of results. The Hortvet and West method for alc. in lemon and orange ext. (*C. A.* **3**, 1189) was recommended for official adoption in view of satisfactory collaborative results. Study was made of *lemon* and *orange oils* and it was found that the specific rotation of these oils varies with the solvent employed, kerosene solns. giving values agreeing well with true polarization. Concd. solns. in alc. give results nearer true polarization than dil. solns. A table showing the effects of 18 different solvents on polarization is given. The polariscopic method for lemon oil in ext. gives results which may vary from −4 to +10%, av. error on 14 samples being +1.2% with max. negative and positive error being −3.2 and +5%. Av. error on 3 orange exts. was +1.2%. The Mitchell factors for calcg. oil from polariscopic reading were found to be well chosen and to be within 0.2% of the truth. (Cf. *C. A.* **14**, 3285). H. A. LEPPER

Errors in gravimetric vanillin determinations in vanilla extract. H. J. WICHMANN. U. S. Food and Drug Inspection Sta., Denver, Colo. *J. Assoc. Official Agr. Chem.* **4**, 479–82(1921).—In the gravimetric detn. of vanillin in vanilla ext. the errors due to contamination with brown gummy residue and failure of petr. ether properly to correct the error as pointed out by Hiltner (*C. A.* **7**, 185 (the reference in this abstract should read *Bull.* **152**, 127) and Bur. Chem., *Bull.* **162**, 82) have again been emphasized. Pure *vanillin* was prepd. and found to leave a residue when sublimed in air at 105°. Error due to non-volatile residue when using the sublimation method for vanillin detn. is 5% too low, which is small in case of standard vanilla ext. but appreciable in reënforced flavors. H. A. LEPPER

The sweetening power of artificial sweeteners. J. GROSSFELD. *Z. Ges. Kohlensaüre Ind.* No. 15, 253(1921); *Ann. fals.* **14**, 289(1921).—The reason for the very high sweetening power possessed by compds. of entirely different constitutions is as yet unknown. Their flavor differs distinctly from that of sugar, especially when the soln. is not too dil. The sweetening power is not const. and varies enormously with the dilu. So far, saccharin has been considered 450 times as sweet as sugar and dulcin 250 times. Their sweetening power, as compared with sugar, is 200–700 and 70–350 resp., being greater in more dil. soln. A mixt. of dulcin and saccharin is much sweeter than either of the constituents alone. A. P.-C.

Definitions and units of measure in the chemistry of sweeteners. THEODOR PAUL. Münich. *Chem.-Ztg.* **45**, 705–6(1921).—Degree of sweetness (*ds.*) is defined as the no. which indicates how many g. of sucrose must be dissolved in a definite vol. of H_2O to produce a soln. of the same sweetness as 1 g. of sweetener (*s.*) in the same vol. Prep. for a group of persons (20–30) 2 solns. of *s.*, one more and one less sweet than a 3% sugar soln. (30 g. per l.). Introduce a series of solns. of *s.* of same concn. differences ranging between these 2. Compare each soln. with sugar soln. twice. Record the verdicts

of sweeter, equal, uncertain and weaker solns. and calc. by the method of Spaerman and Wirth. With saccharin, 55 mg. per l. (1 g. in 18.2 l.) is as sweet as a 3% sucrose soln. For saccharin *ds.* (30 g. sucrose/1 l.) = 546 as 18.2 l. of 3% sucrose contains 546 g. A table shows that the *ds.* of *saccharin* and *dulcin* decrease with increase of concn. as *ds.* for 20 g. sucrose/1 l. are 667 and 364 and for 100 g. sucrose/1 l. are 187 and 70, resp. The *ds.* of glucose and probably other sugar substances do not change with concn. (2–10%) with sucrose = 1, glucose = 0.26, dextrose 0.52, levulose 1.03, lactose 0.28, and mannose 0.42. The mol. degree of sweetness (*mds.*) is the number of mol. wts. of sucrose necessary in a definite vol. of H_2O to produce a sweetness = 1 mol. wt. of *s.* in same vol. and is calcd. by multiplying *ds.* by the mol. wt. of *s.* and dividing by the mol. wt. of sucrose. A table of *mds.* of saccharin and dulcin at concns. from 20 g. sucrose to 100 g. per l. is given. To answer the question in practice, how much artificial *s.* is necessary to replace sugar, P. proposes a "unit of sweetness" (*us.*) which is the no. of g. of *s.* in a definite vol. of H_2O necessary to produce a soln. as sweet as that of 1 kg. of sucrose in the same vol. This *us.* is const. for glucose and probably for other carbohydrates above mentioned, but for saccharin and dulcin it decreases with increase in concn. The *us.* of saccharin and dulcin for 1 kg. sucrose per 50 l. are 1.50 and 2.75 and for 1 kg. sucrose per 10 l. 5.35 and 14.29, resp. A table showing other concns. and examples of practical applications are given. H. A. Lepper

Report on dairy products. Julius Hortvet. St. Paul, Minn. *J. Assoc. Official Agr. Chem.* 4, 482–91(1921).—Collaborative study of methods for detn. of fat in dried whole, skimmed and malted milk led to no definite conclusions. Further study of the methods tried: alkaline-acid modification and neutral Roese-Gottlieb, and direct Et_2O extn. methods was recommended. Cf. *C. A.* 15, 904. H. A. Lepper

The nutritive value of milk in light of modern research. J. Grossfeld. *Umschau* 25, 460–1(1921).—Milk is held as the most necessary food, especially for children, in view of its protein, sugar, fat, mineral and vitamine content. H. A. Lepper

The cryoscopic examination of milk. Julius Hortvet. St. Paul, Minn. *J. Assoc. Official Agr. Chem.* 4, 491–8(1921).—A study of the cryoscopic method was made on over 500 samples of market milk and samples of known origin and compn., including watered samples. The method was found to be a dependable means of detg. with a reasonable degree of accuracy, % of added H_2O in milk (cf. *C. A.* 15, 1359). H. A. L.

Approximate molecular constant of the milks of Montpellier. Fonzes-Diacon. Faculty of Pharmacy, Montpellier. *Ann. fals.* 14, 271–6(1921).—F.-D. calcs. Bouin's approx. mol. const. (g. lactose per l. + 5 × (g. ash per l.)) (cf. Bouin, *Compt. rend. soc. biol.* 83, 1635(1920)) for a large number of milks analyzed by Cazalet (*Thesis* 1918, Montpellier) and by Hugues (*C. A.* 15, 3693). The variations of this "const." are of the same order as those of Mathieu and Ferré's "simplified mol. const." (cf. *C. A.* 8, 2908–9); but it is affected by the breed of cattle, while according to Sirot and Joret (*Ann. fals.* 9, 425(1916)) and Cazalet the latter is not. If Bouin's const. is to be used, it would be better to change it to (g. lactose per l. + 3 × (g. ash per l.). Watering should then be suspected if the const. falls below 69. A. P.-C.

The determination of lactose in the presence of other reducing sugars. H. L. LeGrand. *Ann. fals.* 14, 268–9(1921); cf. *C. A.* 15, 3693.—In the *detn. of monoses in the presence of reducing bioses* by means of Barfoed's reagent, under certain conditions basic salts. ppt. out. One of the factors to be taken into account is the presence of alkali and alk.-earth salts. Milk contains over 0.3% NaCl, and must be dild. so that the alkali salts have a concn. of not over 0.1%. With milks preserved with $K_2Cr_2O_7$ the following method was used for dilg. The milk was defecated with $Hg(HSO_4)_2$, and the excess was pptd. by adding sufficient $Ba(OH)_2$ soln. to dil. the milk to twice or thrice its original vol. The excess of $Ba(OH)_2$ is then pptd. by a current of CO_2. A. P.-C.

Work of the chemist in margarine manufacture. H. P. TREVITHICK. *Chem. Age* (N. Y.) 29, 361–3(1921); *Am. Food J.* 16, No. 9, 19–20(1921).—The work of the chemist in the margarine industry is discussed with respect to the inspection of raw products, factory control and waste elimination and research with respect to maintenance of quality. H. A. LEPPER

Cheese-making experiments. ANON. California Expt. Sta., *Ann. Rept.* 1919, 76.—Cottage cheese can be made from skim milk by pasteurizing at 145° F., cooling and adding starter. Fourteen hours later the curd is cut, cooked at 93° F., drained and salted. 17–19 lbs. of cheese can be obtained from 100 lbs. skim milk. With gassy milk a pure culture of *Bacillus bulgaricus* is more effective as a starter than *B. lactus acidi*. Pepsin and curdalor used as rennet substitutes cause corkiness. A mixt. of one-half rennet and one-half pepsin gives satisfactory results. WILLIAM HAZEN

The cause of eyes and characteristic flavor in Emmenthaler or Swiss cheese. JAMES M. SHERMAN. *J. Bact.* 6, 379–91(1921).—Bacteria capable of fermenting lactates with the production of volatile acids have been found constantly present in cheese of the Emmenthaler or Swiss type in numbers exceeding 1,000,000 per g. The discrepancies in the results of previous workers are probably explained by a faulty combination of salts in the media used, producing a reaction too acid for optimum growth of the organism concerned. This organism belongs to the group of propionic acid-producing bacteria but appears to differ slightly from the several varieties described in the literature. This organism may be used to ensure the proper ripening of Swiss cheese. J. T. M.

Artificial sweet materials (HOLLEMAN) 10. Saponins and their use (MEYER) 27.

Pectin. T. W. DOELL and L. A. F. MAHS. U. S. 1,385,525, July 26. Pectin-bearing substances such as fruit rinds and cores are boiled in H_2O contg. a small amt. of citric or other acid, a bleaching agent such as cellite and boneblack is added and the mass is filtered to obtain an ext. The clear soln. is treated with $MgSO_4$ or Na_2SO_4 to ppt. pectin and the ppt. is sepd., washed, dried and powdered.

Pectous substances from plant tissues. B. T. P. BARKER. U. S. 1,386,224, Aug. 2. Apples, pears or similar plant tissues contg. pectose and its derivs. are freed from natural acidity by expression of the juice and the residual pulp, after drying, is subjected to the action of steam to render the pectous substances sol. and the latter are then extd. with a solvent, *e. g.*, hot or cold H_2O.

Bread. R. GRAHAM. U. S. 1,387,387, Aug. 9. In prepg. edible tubers for use with flour in bread-making, the tubers are subjected to a gelatinizing and converting action by the addition of barley malt or other malted cereal or malt ext. or similar enzymic material. Rice, peas, beans or lentils also may be similarly treated for use with flour in bread making. Bread of good texture and keeping qualities is obtained from mixed starchy materials treated in this manner, with or without addition of bran or middlings.

Bread. C. J. PATTERSON. U. S. 1,385,842, July 26. In making bread, about 0.0033% of H_2O_2 is added to the dough ingredients to increase their moisture-absorbing capacity without breaking down the gluten. Somewhat larger amts. of CaO_2, MgO_2, Na_2O_2 or K_2O_2 may also be used.

Malted food product. J. W. ALLEN. U. S. 1,385,352, July 26. Meats such as beef or pork are simultaneously treated with a pickling soln., and a malt-contg. substance, *e. g.*, an aq. soln. contg. NaCl, $NaNO_3$ and malt ext.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

Chemical technology as a science. F. SMOLENSKI. *Przemysl Chem.* 5, 1–10, 33–7(1921).—The conception that chemical technology is an entirely independent, well defined science is defended. It should not be considered as a subdivision of chemistry. JOHN M. KENO

The relation of our chemical industry to our national defense. IRVINE L. LENROOT. *J. Ind. Eng. Chem.* 13, 888–9(1921).—An address. E. J. C.

A plan for the development of industrial research in Canada. R. F. RUTTAN. *J. Ind. Eng. Chem.* 13, 876–8(1921).—An address. E. J. C.

Modern developments in war making. WILLIAM J. POPE. *J. Ind. Eng. Chem.* 13, 874–6(1921).—An address. E. J. C.

The development of gas warfare and gas defense. JULIUS MEYER. *Chem.-Ztg.* 45, 753(1921); cf. *C. A.* 14, 2122.—The assertions of Hanslian (*Pharm. Ztg.* 66, 416, 555) that the development of gas warfare and gas defense in the German army was due largely to the efforts of the military druggists are denied by M. G. W. STRATTON.

The development of gas warfare. R. HANSLIAN. *Chem.-Ztg.* 45, 877–8(1921).—Cf. preceding abstract. E. H

American Society for Testing Materials standards. Philadelphia, Pa. 890 pp. 1921.—*Standard specifications* are given for C-steel rails; open-hearth steel girder and high tee rails; splice bars of low-C, medium-C, high-C, extra-high-C, and quenched high-C steel; track bolts of quenched C, and quenched alloy steel; steel track spikes and screw spikes; structural steel for bridges, for buildings for locomotives, for cars, and for ships; structural nickel steel; rivet steel for ships; C-steel bars for railway springs, also for railway springs with special Si requirements, for vehicle and automobile springs; silico-Mn-steel bars for automobile and railway springs; Cr-V-steel bars for automobile and railway springs; helical and elliptical steel springs for railways; elliptical steel springs for automobiles; concrete reinforcement bars of billet steel and of rail steel; C-steel and alloy-steel blooms, billets and slabs for forgings; C-steel and alloy-steel forgings; axles, shafts, and other forgings; quenched and tempered C-steel and quenched and tempered alloy steel for locomotives and cars; C-steel forgings for locomotives; C-steel car and tender axles; wrought solid C-steel wheels for steam railway and for elec. railway service; steel tires; steel castings; lap-welded and seamless steel boiler tubes for locomotives; lap-welded and seamless steel and wrought-iron boiler tubes for stationary service; welded and seamless steel pipes; automobile C and alloy steels; boiler and firebox steel for locomotives; boiler rivet steel; automatic screw stock of cold-drawn Bessemer and of cold-drawn open-hearth steel; commercial bar steels; lap-welded charcoal-iron boiler tubes for locomotives; welded wrought-iron pipe; staybolt, engine bolt and extra-refined wrought-iron bars; refined wrought-iron bars; wrought-iron plates; wrought-iron rolled or forged blooms and forgings for locomotives and cars; foundry pig iron; cast-iron pipe and special castings; cast-iron soil pipe and fittings; cast-iron locomotive cylinders; malleable castings; gray-iron castings; wire bars, cakes, slabs, billets, ingots, and ingot bars of lake copper and of electrolytic copper; spelter; light Al casting alloys; hard-drawn, medium hard-drawn and soft or annealed Cu wire; tinned soft or annealed Cu wire for rubber insulation; bare concentric-lay Cu cable; high-strength bronze trolley wire; Mn-bronze ingots for sand castings; the alloy: Cu 88, Sn 10, Zn 2%; bronze bearing metal in ingot form; bronze bearing metals for turntables and movable railroad bridges; solder metal; Cu plates for locomotive fireboxes; Cu bars for locomotive staybolts; seamless boiler tubes of Cu and of brass; brass forging rod; free-cutting brass rod for use in screw machines; cartridge brass; cartridge brass

disks; naval brass rods for structural purposes; high sheet brass; portland cement; natural cement; drain tile; paving brick; building brick; clay sewer pipe; cement-concrete sewer pipe; gypsum plasters; fire tests of materials and construction; purity of raw and of boiled linseed oil from North American seed; purity of raw tung oil; materials for cement grout filler for brick and stone block pavements; materials for cement mortar bed for brick, stone block and wood block pavements; foundry coke; yellow-pine bridge and trestle timbers; southern yellow-pine timber to be creosoted; southern yellow-pine piles and poles to be creosoted; wooden paving blocks *for exposed pavements. Standard methods* are given for *testing magnetic properties of iron and steel;* chem. analysis of plain C steel and of alloy steels; sampling and analysis of pig and cast iron; battery assay of Cu; chem analysis of pig lead, of spelter, of alloys of Pb, Sn, Sb and Cu, of Mn-bronze, of gun metal; test for refractory materials under load at high temps.; test for porosity and permanent vol. changes in refractory materials; test for softening point of fire-clay brick; ultimate chem. analysis of refractory materials, including chrome ores and chrome brick; test for unit wt. of aggregate for concrete; making and storing specimens of concrete in the field; testing shellac; test for flash point of volatile inflammable liquids; routine analysis of white pigments, of dry red lead, and of yellow, orange, red and brown pigments contg. Fe and Mn; testing lubricants (d., free acid, C residue, viscosity); test for abrasion of road materials, for toughness of rock, for apparent d. of coarse aggregates, and of sand, stone and slag screenings, and other fine non-bituminous highway materials; test for quantity of clay and silt in gravel and in sand for highway construction; mechanical analysis of sand or other fine highway material, except fine aggregates used in cement concrete; mechanical analysis of broken stone or broken slag, except aggregates used in cement concrete; mechanical analysis of mixts. of sand or other fine material with broken stone or broken slag, except aggregates used in cement concrete; form of specification for certain commercial grades of broken stone; test for sol. bitumen, for penetration of bituminous materials, for loss on heating of oil and asphaltic compds., for distn. of bituminous materials suitable for road materials; test for softening point of bituminous materials other than tar products (ring-and-ball method) and of tar products (cube-in-water method); sampling coal; lab. sampling and analysis of coal and of coke; sampling and analysis of creosote oil; testing cotton rubber-lined hose; testing cotton fabrics; mechanical testing of metallic materials. *Standard definitions* are given for terms relating to wrought-iron specifications; terms relating to sewer pipe; clay refractories; terms relating to paint specifications; terms relating to materials for roads and pavements; terms relating to structural timber; definitions and rules governing the prepn. of micrographs of metals and alloys. *Recommended practice* is given for annealing of miscellaneous rolled and forged C-steel objects; annealing of C-steel castings; heat treatment of case-hardened C-steel objects; laying sewer pipe. E. H.

The effect of temperature on some of the properties of materials. F. C. Lea. *Engineering* 110, 293–8(1920).—The results of expts. conducted in a non-inductively wound elec. furnace are given. They are of special importance to the builder and engineer. The tests include the detn. of the Brinell number, breaking strength, elastic limit, yield point, modulus of elasticity, elongation and reduction of area at fracture of the following metals between 0° and 900°: delta metal, Mn-bronze, gun metal, nickel-copper, Muntz metal, Al piston alloy, various Cu alloys and a few other substances such as neat cement, steel and reinforced concrete. The effects of varying the temp. gradient and of reheating are also shown. The results are given in curves and some photomicrographs of the treated materials are shown. P. D. V. Manning

Determination of the percentage of dilution of lubricants for internal-combustion engines. C. M. Larson. *Sci. Lubrication* 1, June, 16–7(1921).—A description is given

of 3 methods for the detn. of dilu. of lubricants for internal-combustion engines, with kerosene or gasoline. Two of the methods are comparative with known synthetic blends, one through distn. temp., and one through viscosity. The third is a distn. method which, while the most accurate, requires 1000 cc. of diluted oil. D. K. F.

Process for the evaporation, concentration and drying of all organic or mineral substances. A. SARTORY, L. SCHEFFLER, P. PELLISSIER AND C. VAUCHER. *Compt. rend.* 172, 744–6(1921).—A process for evapn. or removing water from substances consists essentially of passing air over refrigerating coils to remove the moisture, then through a beater to bring it to the desired temperature and finally through a long tunnel in which the substance to be dried is placed on screens. These are moved so as to insure thorough contact with the dry air and can be fixed at will. The app. is said to be especially applicable to the drying of *meat* and *vegetables*. A diagram is given.

P. D. V. MANNING

Preparation of viscous lubricating oils from coal tar. F. SCHREIBER. *Z. angew. Chem.* 34, Aufsatzteil, 425–6(1921).—In 1918 Germany made 50,000 tons of lubricants from the liquors remaining after removing the solids from the anthracene fraction of coal tar. An improved product now available is dehydrogenated and polymerized by means of S. It compares favorably with petroleum oils of the same class (viscosity 4.5 Engler at 50°), except where high temp. is a factor. ERNEST W. THIELE

Grinding. C. J. SEAMAN. *J. Oil Colour Chem. Assoc.* 4, 29–44(1921).—An illustrated address. E. J. C.

Some applications of capillary and electrocapillary chemistry (LEWIS) 2.

Non-inflammable volatile liquid mixture for refrigeration or other uses. A. HENNING. U. S. 1,386,497, Aug. 2. A mixt. of MeCl and MeBr, equal pts., is used for solvent or refrigerating purposes. Cf. *C. A.* 15, 1954.

Lubricant. R. MCLEOD. U. S. 1,387,437, Aug. 9. A lubricating mixt. adapted for use on plug cocks or valves is formed of tallow 1 and rubber 8 parts.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

The economic production of distilled water for large central thermal stations. J. LELEU. *Chaleur et industrie* p. 75 (Feb. 1921); *Industrie chimique* 8, 321(1921).—In large thermal stations distd. H_2O is fed to the generators to prevent scaling, and consequent decrease in efficiency of the tubes. The app. described is a Kestner automatic blow-off evaporator in which the vertical tubes are heated, either by the exhaust from the feed pumps, or by steam taken from a medium-pressure stage of the turbines. Ebullition takes place in a chamber above and at the side of the tubes, the feed water being admitted at the point where the steam enters this chamber. The latter is dried before being sent to the surface condenser. The feed water which is thus instantaneously evapd. loses its mineral impurities; these collect in the lower conical portion of the chamber, whence they are periodically drawn off. The condensate from the heating steam is added to that from the condenser. This process is practical only if the make-up water is not more than 8% of the total feed water. A. P.-C.

Insuring the purity of Plattsburg's water. METCALF AND EDDY. *Public Works* 51, 264(1921).—In a report to the city, M. and E. recommend cleaning shallow reservoirs, dosing with $CuSO_4$ to remove algae and use of liquid Cl to sterilize water. L. P.

Water purification at Toledo. R. W. FURMAN. *Ann. Rept. Toledo Division Water* 1920; *Public Works* 51, 276.—Twenty-two new filters were added in 1920,

Changing from $Al_2(SO_4)_3$ to lime and iron as coagulants produced filter incrustation. A larger settling basin is recommended. LANGDON PEARSE

Gastonia's water improvements. W. A. HARDENBERGH. *Public Works* **51**, 23–3(1921).—This is an engineering description of the improvements made for a mill town of 25,000 population. A novel strainer system in the rapid filters consists of a false bottom contg. ¼-inch glass tubes, 3 in. center to center. LANGDON PEARSE

The significance of hydrogen-ion concentration in water purification. H. P. EDDY. New Eng. Water Works Assoc. *Eng. Contr.* **56**, 354–5(1921).—E. defines the meaning of H-ion concn. and its effect on the reaction of coagulants in water purification. Expts. are suggested on control of the p_H to det. effect on passage of $Al_2(SO_4)_3$ through filters, prevention of corrosion, control of microörganisms, and increase in efficiency of operation. LANGDON PEARSE

Method of clarifying stagnant water, especially in ponds and lakes. C. T. DOWELL. Oklahoma Agr. Expt. Sta., *29th Ann. Rept.* 1920, p. 46.—Twenty-five lbs. of $CuSO_4$ to the acre of water, 4 ft. in depth is a satisfactory amt. for clarification of water. The $CuSO_4$ should be distributed so as to come in contact with as much of the pond water as possible. J. J. SKINNER

Boiler-feed water and its modern purification methods. E. J. TOBI. Amsterdam. *Chem. Weekblad.* **18**, 462–3(1921); cf. *C. A.* **15**, 3163.—Criticism of an article on the Neckar-process as described by the firm of Muller of Stuttgart. V. V.

Degassing and purification of boiler water. PAUL KESTNER. Paris. *Proc. Inst. Mech. Eng.* 1921, No. 4, 291–330. Discussions. *Ibid* 330–60.—See *C. A.* **15**, 1588. C. J. WEST

Sewage treatment at Allentown. H. F. BASCOM. *Public Works* **51**, 269–72 (1921).—This is an engineering description of an electrolytic plant using lime, followed by settling. The bacterial removal averages 99.3%. One unit is run about 2 hrs. per 24 hrs. LANGDON PEARSE

Treating of city sewage. G. A. JOHNSON. *Can. Eng.* Sept. 22, 29(1921).—J. gives his opinion of the usual methods of sewage treatment, largely from the standpoint of their weaknesses and recommends activated sludge and an electrolytic process using Fe plates and lime. Only bacteriological results are given on the latter process. LANGDON PEARSE

Imhoff tank experiences in America. PETER GILLESPIE. *Can. Eng.* Oct. 6(1921). —G. reviews a decade of operation, covering 30 plants. Most tanks produce inoffensive sludge easily dried. The principal trouble has been foaming. Agitation of sludge once a week and ample sludge capacity (2 cu. ft. per person in sep. systems, 3 cu. ft. on combined systems) are recommended. LANGDON PEARSE

The prevention of smoke pollution. LEONARD HILL. *J. Roy. San. Inst.* **42**, No. 2, 41–4(1921); *Public Health Eng. Abstr.* Oct. 8 (1921).—Through stopping the evapn. of water and warming of the ground by cutting off the radiant energy of the sun, smoke greatly increases the cold and dampness of the English climate and impels people indoors, to indoor occupations and pleasures in place of healthy outdoor exercise. The deleterious effects so produced are of greater significance than the blackening of the lungs by inhaled soot. A plea is made for the production of smokeless fuel at a cheapened cost. G. C. BAKER

Smoke abatement. J. S. OWENS. *J. Roy. San. Inst.* **42**, No. 2, 44–51(1921); *Public Health Eng. Abstr.* Oct. 8 (1921).—O. presents data regarding the conditions over London. The largest single factor is the domestic fires of the city. Between the hours 6 A. M. and 9 A. M. over 200 tons of soot are produced; a dense smoke fog extending over the whole of London and up to a height of 400 ft. will contain about the same amt.

of soot. Discussion brought out various remedies to abate smoke nuisances due to domestic fires. G. C. BAKER

Practical hygienic efficiency of the Palmer apparatus for determining dust in air. H. F. SMYTH AND M. ISZARD. *J. Ind. Hyg.* 3, 159–67(1921).—This is a reply to criticisms offered by Bill (*C. A.* 14, 508) and Katz, Longfellow and Fieldner (*C. A.* 14, 3388) concerning the efficiency of the Palmer water-spray method of dust sampling. Results of actual dust studies are given. The size of the dust samples found in animal lungs agree with the results of other experimenters. Particles about 1 micron in diam. are the most frequent, while 60–80% of the countable particles range from 1 to 5 microns. The Palmer method when sampling air with dust particles up to 40 microns at a rate of 5 cu. ft. per min. is at least 1.33 times as efficient as the modified Palmer app. used by both Bill and Katz and run at 4 cu. ft. per min. The efficiency of the original Palmer app. at 5 cu. ft. per min. rate is 82% by wt., making it the most efficient dust-sampling device known for industrial hygienic tests. MARTIN FLENTJE

Causes of typhoid fever in New York City. L. I. HARRIS. N. Y. City Dept. Health, *Bull.* Aug. (1921); *Eng. Contr.* 56, 346(1921).—Of 969 cases in 1920, 42 were traced to shellfish. 85 chronic typhoid carriers were recorded. LANGDON PEARSE

The equilibria of permutites (HISSCHEMÖLLER) 2.

Degreasing garbage. F. DANKS. U. S. 1,386,165, Aug. 2, Garbage is degreased in containers mounted on a circular track and having a steam supply near their bottom and an overflow outlet for floating grease.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER AND ALBERT R. MERZ

Nitrification in acid soils. R. E. STEPHENSON. Iowa Expt. Sta., *Research Bull.* 58, 331–49(1920).—Nitrification may take place in acid soils. The addition of CaO produced no measurable effect on the nitrification of the original soil N, but it did cause a marked increase in the nitrification of $(NH_4)_2SO_4$ added to the soil. Though very large amts. of CaO may increase the nitrifying power of a soil, only that necessary to neutralize the most active acids (as shown by a detn. of the CaO requirement) is essential for adequate nitrification and max. crop production. WILLIAM HAZEN

Increase in the number of Clostridium pastorianum (Winogradski) in soils partially sterilized by calcium sulfide. G. TRUFFAUT AND N. BEZSSONOFF. *Compt. rend.* 172 1319–22(1921).—When soils have been partially sterilized by heat and CaS and dil. solns. of these soils are introduced into tubes of glucose agar, fermentation will take place oftener than when the agar is inoculated with untreated soil. The number of *Clostridium* found in the soil is approx. 100,000 per g., which is 10 times as great as the number of *Azotobacter*, as given by Jones and Murdock. It appears, therefore, that *Clostridium pastorianum* and not *Azotobacter* is the principal agent for the fixation of N in the soil. WILLIAM HAZEN

Representative Transvaal soils. B. J. SMIT. *J. Dept. Agr. Union S. Africa* 2, 170–6(1921).—Tables show the mechanical and chem. compn. and the results of fertilizing expts. on various types of soils. The conclusions are: (1) On the quartzite soils the best fertilizer is one contg. phosphates in the form of basic slag. (2) For supplying N leguminous crops should be grown, since they also improve the soil by supplying org. matter. C. B. DURGIN

The manuring of vineyards. J. C. ROSS AND S. W. VAN NIEKERK. *J. Dept.*

Agr. Union S. Africa **2**, 163–9(1921).—System of fertilizing and the time and methods of application are described. CaO is considered a soil improver rather than a fertilizer and its useful functions are outlined. C. B. DURGIN

Loess and black soil in the region of Vienna. WILHELM GRAF L. ZU LEININGEN. *Intern. Mitt. Bodenk.* **10**, 118–29(1920).—The loesses of the region of Vienna contain large amts. of $CaCO_3$, av. about 37.0% $CaCO_3$. Even in the decomposed strata the CaO content is high. Black soils contain much mica and a relatively large amt. of CaO. Partial analysis of a typical black soil shows the following compn.: humus (Knop method) 9.59, loss on ignition 16.5, HCl-sol. CaO 1.22, MgO 0.127, Al_2O_3, Fe_2O_3, and P_2O_5 8.87%. The geology of the region is discussed. M. S. ANDERSON

The "alkali" content of soils as related to crop growth. F. T. SHUTT AND ALICE H. BURWASH. Ottawa. *Trans. Roy. Soc. Canada* **14**, Sect. III, 57–70(1920).—A progress report. Cf. *C. A.* **14**, 2525. A. T. CAMERON

The influence of water content and void spaces on the workability of soils. HANS ZANDER. *Intern. Mitt. Bodenk.* **10**, 89–117(1920).—Formulas are given and some results plotted showing the relationship between water-holding power, void vols. and cohesion in different types of soil. M. S. ANDERSON

The infiltration of water in agricultural soils. C. HUGUES. *Giorn. risicoltura* **9**, 74–8(1919). *Bull. Agr. Intelligence* **10**, 1077–8.—A lab. research app. is described for measuring the more or less variable capacity of soils for allowing water to percolate down from the surface to the more deeply seated layers. The principle upon which the app. is constructed is to allow water to descend automatically from a Mariotte flask into a tube filled with the soil to be tested. This water then flows through a small tube, which passes through the hermetically closed lower opening of the tube into another Mariotte flask. The rapidity with which the water descends through a given distance of the column of soil in a tube of known diam. is then measured under const. exptl. conditions for the different samples of soil. A comparative examn. with this app. of different samples of soil shows that the smaller the vol. of the soil particles and consequently that of the capillary pore space, the more slowly does the water pursue its downward course. In the case of a clay soil with 42.83% of pore space it took 113 hrs. 42 min. for the water to reach the lower opening of the tube, whereas the water percolated through a sample of alluvial soil with 57.36% interstices in 96 hrs. 18 min. With the same sample of soil the time taken to reach the bottom of the tube with water, 1% and 25% Na_2CO_3 soln. amounted, resp., to 39 hrs. 18 min., 32 hrs. 45 min. and 28 hrs. The rapidity of the descent in the soil, therefore, increases with the concn. of the soln. W. H. ROSS

Soil reaction and choice of fertilizers. R. GANS. *Intern. Mitt. Bodenk.* **10**, 186–96 (1920).—The choice of fertilizers should be detd. by the reaction of soil as well as the physiol. effect on particular plants. Neutral salts produce a basic exchange in soils which is only slightly reversible. The acidity from inorg. constituents of soil arises from a breaking down process in which hydrates of SiO_2 and Al_2O_3 are formed as well as by the oxidation of FeS. The nature of the mixt. formed from the parent rock is indicated by the acidity produced through the action of neutral salts such as KCl and Ca acetate on the decomposed rock material. Mol. mixts. of SiO_2 and Al_2O_3 hydrates formed from the parent rock by leaching are capable of producing the strongest acidity while mixts. not mol. and yet intimate produce somewhat smaller amts. of acid. Gross mixts. formed through long weathering of parent rocks of unequal solubilities give rise to little acidity. M. S. ANDERSON

The utility of the star-fish as fertilizer. A. VACHON. *Trans. Roy. Soc. Canada* **14**, Sect. V, 39–49(1920).—Analyses of two species of star-fish are given. It is considered that they can be usefully employed as fertilizer when a supply can be obtained in the

vicinity. On account of their content of $CaCO_3$, they are especially beneficial to acid soils. Their K content is negligible. A. T. CAMERON

The influence of fertilization and spacing upon the yield and composition of sugar beets. M. GERLACH. *Blätter Zuckerrüb.* 28, 123–9(1921).—Results show the favorable influence upon the yield of beets of the application of mineral salts, especially N and K compds., both alone and with stable manure. Extensive expts. showed an av. sugar content of 17.9% in beets grown on soil untreated or treated with stable manure; application of both stable manure and a moderate amt. of mineral fertilizer gave a content of 18.7%. Another series of expts. gave the following av. contents: full mineral fertilizer, 18.4%; without N, 18.6%; without phosphate, 18.1%; without K, 17.9%. The results indicate a lower content of sugar in beets grown further apart. P. R. D.

The Beccari fermentation chambers. V. RACAH. *Italia Agr., Giorn. Agr.* 56, 242–7(1919); *Bull. Agr. Intelligence* 10, 1233–6.—A detailed description is given of the construction and method of operation of the Beccari fermentation chambers for the treatment of barnyard manure and the rotting of household and street rubbish. The most varied kinds of rubbish when treated in the Beccari chambers yield a product of fairly const. fertilizing value contg. an av. of N 0.34, P_2O_5 0.37, and K_2O 0.64%. Street sweepings undergo abs. sterilization in the chambers, owing probably to the combined action of the high temp., moisture, nascent gases and biol. conflict between the different germs. W. H. Ross

The solution of the nitrogen problem. H. M. NAGANT. *Sci. Agr.* 1, 184–5, 230–3, 274–7; 2, 33–5(1921).—A review of the role of N in agriculture, and of the progress that has been made in the com. fixation of atmospheric N. W. H. Ross

Insecticides and fungicides for farm and orchard crops in Massachusetts. E. B. HOLLAND, A. I. BOURNE AND P. J. ANDERSON. Mass. Agr. Expt. Sta., *Bull.* 201, 1–37(1921).—This bulletin treats of the compn. of insecticides and fungicides, the conditions under which the various materials and mixts. are effective, presents tables showing standard formulas for application, a diagram showing safe and dangerous mixts. of materials, and finally a table showing the guarantees of a number of proprietary articles. W. H. Ross

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Origin of African phosphates (FAERGA) 8. Phosphate industry. I. Sources of supply of mineral phosphate (PACKARD) 8.

Fertilizer. J. C. HECKMAN. U. S. 1,386,331, Aug. 2. A fertilizer is prepd. by dissolving blast-furnace flue dust or Fe oxide in H_2SO_4 and substantially neutralizing the soln. with granulated blast-furnace slag.

Treating "lime nitrogen." J. M. A. STILLESEN. U. S. 1,386, 445, Aug. 2. "Lime nitrogen" is treated with H_2O and CO_2 in order to change CaO present into basic carbonates.

16—THE FERMENTATION INDUSTRIES

H. S. PAINE

Microörganisms and some of their industrial relations. A. C. CHAPMAN. *J. Roy. Soc. Arts* 69, 581–9, 597–605, 609–19(1921).—C. has reviewed the subject indicated in the title in a very interesting manner. The paper begins with the work of Buchner on zymase and reviews the well known contributions of Harden to *alc. fermentation*. The theories of alc. fermentation are mentioned. The biol. manuf. of *glycerol* is described. *Saccharomyces ellipsoideus* was used to ferment Porto Rican "black strap" molasses. The fermentations were conducted at 30–32° and occupied 5 days. The

amylo process for the production of alcohol is also described. This involves the saccharification of grains by means of molds. Citric acid manuf. by means of molds such as *Aspergillus niger* and *Mucor pyriformis* acting on glucose is mentioned. The biology of lactic acid, citric acid, acetic acid, butyl alc., and acetone manuf. is also discussed.
F. W. TANNER

Fermentation without yeast (BAUER, HERZFELD) 11A.

Acetone and butyl alcohol by fermentation. E. RICARD. U. S. 1,385,888, July 26. See Brit. 130, 666 (*C. A.* 14, 90).

Dry yeast. W. B. D. PENNIMAN. U. S. 1,386,359, Aug. 2. Moist yeast is mixed with starch or flour and with a smaller amt. of glucose or dextrin, and to this mixt. there may be added small amts. of sol. inorg. salts such as NH_4 phosphate, KNO_3 or Mg phosphate and the mixt. is dried at a low temp. *in vacuo*. U. S. pat. No. 1,386,360 relates to a similar method, in which the dextrin or glucose may be omitted. U. S. pat. No. 1,386,361 covers the prepn. of a dry yeast product by first propagating yeast in a barley malt wort contg. wheat flour, then thickening the liquid culture with corn meal to form a soft dough, granulating the latter and drying *in vacuo* until the moisture content is reduced to about 10%.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

The purity of commercial tyrosine. A. BERTHELOT AND MLLE. OSSART. *Bull. soc. chim. biol.* 3, 247(1921).—Of 6 prepns. examd. only 2 were approx. pure. The others contained in one instance traces of Ba, and in most cases varying amts. of cystine.
A. T. CAMERON

Medicinal plants and fluidextracts. C. INVERNI. *Boll. chim. farm.* 60, 281–4 (1921).—Although fluidexts. are continually being added to the pharmacopeias of other countries, the Italian Pharmacopeia still recognizes only 4. This lack of legal standard accounts for the fact that the 10 fluidextracts of domestic manuf. assayed by I. show less than half the alkaloidal content of similar fluidextracts of foreign manuf.
A. W. DOX

The use of denatured alcohol for surgical purposes. CARAVITA FRANCESCO. *Boll. chim. farm.* 60, 285–7(1921).—Alc. used in hospitals is subject to the federal tax in Italy. A plea is made for the introduction of a specially denatured alc. for surgical purposes, since the MeOH and pyridine ordinarily used for denaturing are objectionable.
A. W. DOX

Determination of alcohols and phenols in ethereal oils by acetylation with pyridine (especially santalol, menthol, eugenol). H. W. VAN URK. *Pharm. Weekblad* 58, 1265–9(1921).—The method of Verley and Bölsing (*Ber.* 34, 3354) which makes use of pyridine in place of NaOAc in the acetylation of alcs. and phenols with Ac_2O, although more rapid, is less accurate than the usual method. With menthol it gives low and discordant values. The best results are obtained with eugenol, although these are usually low. The method is applicable to santalol and eugenol for the detection of gross adulteration, especially where economy of time and material is desired. It is not recommended for accurate detn. of santalol, menthol or eugenol.
A. W. DOX

Urotropine. ÉT. DEFRANCE. *J. Pharm. Belg.* 3, 605–8(1921).—*Action of ammonium salts on urotropine.* The action of NH_4 salts on $N_4(CH_2)_6$ is analogous to the action of NH_4 salts on CH_2O. On heating a mixt. of NH_4Cl and $N_4(CH_2)_6$ a black mass is finally obtained. This material is sol. in H_2O and alkalies and has the odor of

the methylamines. The reaction may be used to det. adulteration of $N_4(CH_2)_6$ with NH_4 salts. Samples contg. 0.5–1.625% of NH_4 salts become yellow on heating, those contg. 2.5 to 3.25% become brown, and those contg. 4.8% and over become black. *Action of acids (especially HCl) on urotropine.* In the presence of H_2O, alone, HCl reacts with $N_4(CH_2)_6$ in a normal manner, NH_4Cl and CH_2O being the products formed. The addition of EtOH in the proportion $N_4(CH_2)_6$ 1 mol. (28 g.), EtOH 12 mol. (140 cc.), HCl 4 mol. (80 cc.) causes $CH_2(OEt)_2$ to be formed as one of the reaction products. With H_2SO_4 under similar conditions, only a small amt. of acetal is obtained. This is thought to be due to a partial transformation of the latter into $EtHSO_4$. With AcOH, the reaction does not take place until the mixt. has been boiled for 10 min. The products obtained by the action of HCl in the absence of H_2O are identical with those obtained when an NH_4 salt is heated with $N_4(CH_2)_6$. The action of HCl gas in the presence of an anhydrous solvent (abs. EtOH, Et_2O or petr. ether) results in the formation of a hydrochloride of $N_4(CH_2)_6$, only a very small amt. of $CH_2(OEt)_2$ being produced. *Action of phenols on urotropine.* If the EtOH is replaced by PhOH in the HCl mixt. described above, an acetal of the formula $CH_2(OPh)_2$ and are sinous condensation product are obtained. In the absence of HCl, a phenate of the probable formula $N_4(CH_2)_6 \cdot 4C_6H_5OH$ is produced. On satg. a soln. of CH_2O with $C_6H_4(OH)COOH$ in an excess of NH_3, a ppt. is obtained which contains neither $N_4(CH_2)_6$ nor NH_3. On fusing a mixt. of thymol 4 mol. or eugenol 4 mol. with 1 mol. of $N_4(CH_2)_6$, complete combination is not effected at the end of 1 hr. On fusing guaiacol 4 mol. with 1 mol. of $N_4(CH_2)_6$ for 3 hrs. and cooling, a cryst. mass is obtained which yields a compound of the formula $2MeOC_6H_4OH_3 + N_4(CH_2)_6$ on extn. with Et_2O. Naphthol, on fusion with $N_4(CH_2)_6$, forms a condensation product with the liberation of NH_3. A. G. DuMez

Monographs on floral odors. V. Rose odor. P. P. R. *Perfumery Essent. Oil Record* **12**, 276–9(1921); cf. *C. A.* **15**, 3364.—The subject is treated under the several heads: The rose and its perfume, the rose in the perfume industry, natural otto of rose, synthetic rose perfume, and individual constitutents of otto of rose. The compn. of both the natural and artificial ottos are fully discussed. W. O. E.

Quantitative determination of acetanilide. A. RECLAIRE. *Perfumery Essent. Oil Record* **12**, 280(1921); cf. Turner and Vanderkleed (*C. A.* **1**, 1457), Seidell (*C. A.* **1**, 2401), Emery (*C. A.* **3**, 2344; **4**, 2351), Thonus *Dissert. Leiden* 1918.—The method described for detg. acetanilide in musk prepns. involves boiling the mixt. contg. the acetanilide with HCl, dilg. to 500 cc., treating an aliquot (25 cc.) with 5 cc. concd. HCl and sufficient bromide-bromate soln. (3.4 g. $KBrO_3$ and 13 g. KBr in 1000 cc.) to produce a persistent yellow color, then after the lapse of 15 min. adding 5 cc. 10% KI soln. followed by titration with 0.1 *N* $Na_2S_2O_3$, 1 cc. of which = 0.002252 g. acetanilide. W. O. E.

Constants of chamomile oils. MASSERA. *Rev. ital. essence e profum; Bull. sci. Pharmacol.* **28**, 286; *Perfumery Essent. Oil Record* **12**, 283(1921).—The following consts. are given for freshly distd. Roman color blue becoming green and yellowish green on exposure to air and light; yield 0.8 to 1%; d. 0.905 to 0.920; $[\alpha]_D^{20}$ −3 to +3°; sapon. no. 220 to 320; sol. in less than 1 pt. of alc. and in 3 pts. 70% alc. (turbid soln.); consists of isobutyl and isoamyl esters of angelic and tiglic acids; also an isomer of camphor, anthemol and a paraffin, anthemene. The German oil thickens at +14°; d. 0.920 to 0.955; sapon. no. after acetylation 115 to 250; optically inactive; sol. in 8 to 10 pts. 90% alc.; contains esters of caprylic and nonylic acids, and a paraffin; often adulterated with cedar oil, turpentine or copaiba balsam. W. O. E.

Precautions to be observed in the use of adrenaline in prescriptions. ANON. *Bull. Pharm.; Midland Druggist* **55**, 140–1(1921).—Deterioration of adrenaline solns., usually due to oxidation, is retarded by acids, hastened by alkalies. A trace of strong

acid, *e. g.*, 0.01% HCl referred to total vol., is more efficient than an equiv. amt. of a weak acid, *e. g.*, boric or benzoic acid? Avoid all Fe salts also the use of glass vessels yielding free alkali. When alk. mixts. are prescribed in the form of spray for nose and throat, direct adding the adrenaline soln. immediately before use. Adrenaline is incompatible also with I and with $HgCl_2$. S. WALDBOTT

George Beecher Kauffman, 1855–1921. ANON. *Midland Druggist* **55**, 166–7, 208–11(1921).—An obituary, with portrait, and eulogies by J. H. Beal, John Uri Lloyd, R. H. Bradley, H. M. Whelpley, Simon N. Jones and H. V. Arny. S. WALDBOTT

Dr. F. B. Power. ANON. *Pharm. J.* **106**, 451(1921).—An account of the presentation of the Wellcome Medal to Dr. Power at Washington. S. WALDBOTT

The titration of certain alkaloids. NORMAN EVERS. *Pharm. J.* **106**, 470–2(1921).—The indicators ordinarily employed for the titration of the alkaloids *morphine, quinine* and *atropine* are not the most suitable. From measurements of the H-ion concn. of the solns. of the pure hydrochlorides it was found that *bromophenol blue* is a better indicator for morphine, atropine and the neutral salts of quinine. For the acid salts of quinine, *methyl red* is the most suitable indicator. S. WALDBOTT

The analysis of theobromine sodium salicylate. C. T. BENNETT AND F. B. WINDLE. *Pharm. J.* **106**, 472(1921).—The formula $Na_2C_{14}H_{11}N_4O_4$, *i. e.*, equimol. proportion of the salts, calls for 49.7% theobromine and 38.1% salicylic acid (*S*). The Brit. Pharm. process for the detn. of *theobromine* (*T*) is modified. Dissolve 2 g. of the dried salt in 10 cc. H_2O, add phenolphthalein (*P*) and titrate with *N* HCl. Not more than 5.5 cc. should be required. If the soln. is not slightly alk. to litmus, add 1 or 2 drops of NH_4OH to make it so, allow to stand for 3 hrs. at 15.5°, filter off the *T*, wash with 4 portions of 5 cc. of cold H_2O and dry at 100°. To the wt. of the ppt. add 0.13 g. The % found should not be less than 46.5%. The method agrees in results with that of the U. S. P.; the Brit. Pharm. gives too low results. For the detn. of *S*, put the filtrate from the detn. of *T* into a separator, add 5.5 cc. *N* HCl, shake out with 4 × 10 cc. Et_2O, wash the mixed Et_2O solns. with 10 cc. H_2O, add 50 cc. H_2O to the Et_2O soln. in the separator, and titrate *S* with *N* NaOH, using *P* and shake after each addition. 1 cc. *N* NaOH = 0.138048 g. *S*. A minimum of 37.5% of *S* is suggested. The use of $CHCl_3$ (Squire) gives too low results. Detn. of total combined Na should be made by ignition and conversion into Na_2SO_4; titration of the alkali formed would lower the results.

S. WALDBOTT

Note on liquefied carbolic acid. C. T. BENNETT. *Pharm. J.* **106**, 472–3(1921).—Suitable addition of H_2O obviates crystn. of PhOH in cold weather. In 3 mixts. each of 100 g. PhOH (m. 40.5°) with, resp., 15, 20, 28 g. of H_2O, sp. gr. was, resp., 1.068, 1.064 and 1.060; m. p. after freezing, resp., 8.5°, 6.5° and 2.5–3.0°. The amt. of H_2O that can be added before sepn. occurs, was, resp., 20%, 16 and 7% by wt. Discussion on the diln. in the above proportions is invited. S. WALDBOTT

Determination of small quantities of phosphate in glycerophosphates. J. L. LIZIUS. *Pharm. J.* **106**, 478–9(1921); cf. *C. A.* **14**, 2899.—Amts. of H_3PO_4 less than 0.1% in 0.1 g. glycerophosphate (*G*) give with NH_4 molybdate in presence of dil HNO_3 a yellow color only, whose depth is proportional to the amt. of H_3PO_4 present. Most of the solid com. samples of *G* (*i. e.*, of Na, Ca, Mg) contain very little PO_4, less than 0.1%; only the ferric compd. contained as much as 12.5%; but the sirups of *G* usually contain considerable amts., that of the 75% K compd. 9.5%; of the 75% Na compd. 2.0–4.0%. A reasonable limit for the amt. of phosphate in *G* is 0.1% H_3PO_4. It is tested for as follows: Dissolve 1 g. of *G* in 25 cc. of dil. HNO_3. Five cc. of this soln. added to 10 cc. of 25% HNO_3 and 10 cc. of NH_4 molybdate should not give a deeper yellow color than is given by 5 cc. of a 0.004% soln. of H_3PO_4 added to 10 cc. of 25% HNO_3 and 10 cc. of 10% NH_4 molybdate. S. WALDBOTT

The assay of atropine and cocaine in the British Pharmacopeia ointments. H. J. FOSTER. *Pharm. J.* 106, 479(1921).—A simple method of extg. with HCl from a petr. ether soln. and extg. with $CHCl_3$ after rendering alk. with NH_4OH, failed to give uniform results. Instead, weigh 2 g. of ointment into a 50-cc. beaker, add 10 cc. $CHCl_3$, transfer into a separator, washing the beaker with 10 cc. $CHCl_3$. Now add 20 cc. of 0.05 *N* H_2SO_4, shake and sep., wash the $CHCl_3$ layer twice with 10 cc. H_2O, add this to the acid liquid, then titrate this with 0.05 *N* KOH, using bromophenol blue as indicator. Each cc. is equiv. to 0.01446 g. atropine and 0.01516 g. cocaine. Uniform results are obtained. S. WALDBOTT

The approximate estimation of commercial cresol in lysol. C. J. JORDAN AND F. SOUTHERDEN. *Pharm. J.* 106, 479–80(1921).—Com. lysol is castor or linseed oil soap contg. about 50% cresol. For assay, distil a given wt. of com. cresol with steam, det. wt. of sepd. cresol, add to it the wt. dissolved in the distd. vol. on the basis of a soly. of 1:50. The amt. of cresol used is thus recovered, the results are not affected by addition of castor or linseed oil soaps. Apply the method to 60.70 g. of lysol, to which add 30.35 cc. dil. H_2SO_4, then distil with steam until $FeCl_3$ no longer gives a blue color to the distillate, and proceed as before. In 5 brands of com. lysol, the cresol content varied from 51.8 to 58.8%, in 5 others, from 46.6% to 35.3%. S. WALDBOTT

The assay of colchicum by the phosphotungstic method. EDWARD C. DAVIES. *Pharm. J.* 106, 480–1(1921).—Exhaust 5 g. of the seeds by percolation with 100 cc. of 70% EtOH, evap. off EtOH and take up the residual colchicine with 3 × 20 cc. H_2O, shake out with 20, 15, 15 and 10 cc. of $CHCl_3$. Evap. the combined solvents and ext. the residue with 30 cc. of hot H_2O. Cool, filter and add 3 cc. of phosphotungstic acid soln. (10 g. Na tungstate, 6 g. Na phosphate, 50 cc. H_2O, acidified with HNO_3), then 7 cc. of dil. H_2SO_4. Centrifuge the pptd. phosphotungstate, suspend in H_2O and liberate colchicine, (*a*) by shaking with 30 cc. of $CHCl_3$, with which colchicine forms a compd.; shake again with 10 cc. $CHCl_3$ and evap. to dry const. wt. by the aid of a little EtOH, or, (*b*) decompose the ppt. with 20 cc. $CHCl_3$, *then* (to avoid yellow color) add 10 cc. of $Ca(OH)_2$ soln. or 10 cc. of 1% NH_4OH, then again 10 cc. $CHCl_3$ and proceed as in (*a*). The seeds yielded 0.75% (process *a*) and 0.72% (*b*); the corm 0.38% (*a*) and 0.40% (*b*). The alkaloid is but slightly yellowish, and purer than when obtained by the U. S. P., Brit. Pharm. Codex, or Farr and Wright's methods. With pure colchicine, 97.3% was recovered. S. WALDBOTT

A contribution to the study of digitalis. KARAM SAMAAN. *Pharm. J.* 106, 481–2, 506(1921).—S. compares the relative toxicity and pharmacol. action on the whole heart of the frog of fresh Brit. Pharm. infusion of digitalis with that of digitalis glucosides and various concd. infusions of digitalis, 1 fresh, 2 four weeks old. The tracings (not shown in the article) obtained with a 1:7 diln. of concd. infusion prepd. with 20% EtOH, are comparable with those of the 1:4 dild. Brit. Pharm. infusion. Concd. infusions, whether prepd. with 20% EtOH or with 0.1% $CHCl_3.H_2O$ as in the Brit. Pharm. Codex, are essentially digitoxin prepns., like the tincture, whereas the fresh Brit. Pharm. infusion is essentially a digitalein prepn. Thus, the replacing of the Brit. Pharm. infusion by its "equiv." of the concd. alc. infusion is not justifiable. The ppt. in old infusions also contains digitoxin. Expts. made with a 25-yr.-old concd. infusion (Brit. Pharm. 1885) seems to indicate that all the digitalein and digitoxin present in soln. had decomposed; only that part of the digitoxin that was in the ppt. seems to have resisted decompn. The use of fresh infusion is essential. S. WALDBOTT

Examination of commercial bismuth phenate. C. E. CORFIELD AND G. R. BOYES. *Pharm. J.* 106, 483–4(1921).—This compd., reputed to be an intestinal antiseptic, is given: the compn. $C_6H_4OBi(OH)_2$, contg. 27.89% PhOH and 69.28% Bi_2O_3 (Brit. Pharm. Codex). In 5 com. samples, PhOH was 1.99–4.56%, one had 11.4 and was free

from N, one had traces of PhOH. Bi_2O_3 varied from 81.18 to 86.65%, total N as (NO_3) in 5 samples from 2.35 to 3.38%, due to $BiONO_3.H_2O$ or to $C_6H_4(OH)NO_2$. C. and B. were unable to prep. Bi phenate of the color and chem. compn. required by the Codex. The compd. readily decomposes in acid or alk. soln. A max. phenol content of 14.76% was obtained as follows: Dissolve 60 g. $BiONO_3.H_2O$ in 45 cc. of 70% HNO_3, dil. with 150 cc. H_2O, add this slowly to a soln. of 42 g. NaOH and 20 g. PhOH in 750 cc. H_2O while stirring, filter, wash with cold H_2O and dry in air. The filtrate is neutral, the yield is 58 g. of a white powder, free from N, and contg. 81.93% of Bi_2O_3 and 14.76% PhOH. This compd. evidently differs from that given in the Codex. The com. samples appear to have been made in presence of large excess of HNO_3, resulting in nitration of phenol and formation of dark resinous products. S. WALDBOTT

Action of heat and moisture on the activity of ergot and extractum ergotae liquidum. G. TATE. *Pharm. J.* 106, 485, 505(1921).—The liquid ext. appears to be more susceptible to heat than dry ergot, and moist ergot under favorable conditions is likely to increase in activity; therefore it seems advizable to send out the ergot powdered and dry in air-tight containers. The liquid ext. should be stored at a temp. below 80° F. In discussion it was stated that a certain ext. near deterioration showed increased activity by the blood pressure test; and wormy ergot gave better physiol. results than sound ergot. The cause of the increased activity was probably the decompn. of protein, yielding amino and other acids. S. WALDBOTT

An investigation of some of the factors which may determine the keeping qualities of infundibular extract. G. TATE. *Pharm. J.* 106, 486, 505(1921).—Ext., exposed to direct Hg-vapor light for 1 hr. at 8-in. distance, deteriorated only about 5%; ext. in white or amber glass ampoules retained its activity. As to the effect of heat and acidity, the results of Adams, Fenger and Hull, and Abel and Nagayama (*C. A.* 11, 2206; 14, 2946; 15, 125) are quoted. T. found no decrease of activity in a certain ext. after boiling for 30 min. (the ext. being "thermostable"); nor upon exposure of the same ext. to 38° for 25 days after addition of 0.2 to 2% AcOH in 5 samples. T. thought a thermostable ext. might be serviceable after storing in a tropical climate, *e. g.*, in India, but parallel expts. on samples of the same origin and the same acidity did not bear out this assumption. Keeping such drugs at a temp. not above 80° F. will probably best prevent excessive deterioration. In discussion, the claim of permanency of these exts. on boiling is doubted. The methods of physiol. testing need re-investigation. S. WALDBOTT

Birch tar. E. M. HOLMES. *Pharm. J.* 106, 508(1921).—The genuine Russian oil (*oleum rusci, ol. betulinum;* H., *C. A.* 4, 3274; C. T. Bennett, *Pharm. J.* 85, 4(1910)) is difficult to obtain. To it, *i. e.*, to pyrobetulin, the odor of Russia leather is due; it also has been used in preventing insect stings, and relieving the itching of *eczema papulosum* (*Pharm. J.* [3] 14, 439–40(1883)). H. suggests using the waste bark of English-grown *Betula alba* in the currying of Russia leather, and the manuf. of *betulin anhydride* (*pyrobetulin*), a valuable antiseptic (J. Wheeler, 1894). The bark contains 10–12% of betulin and yields about 33% of tar. Mixing the bark with other barks should be avoided. Possibly India may produce birch tar and betulin abundantly. S. WALDBOTT

Saponins and their use (MEYER) 27. **The nature and composition of Irish-moss mucilage** (HAAS) 11D.

Theobromine from cacao waste. E. DE GROUSSEAU and A. VICONGNE. U. S. 1,386,166, Aug. 2. Cacao waste is agitated with a solvent formed of $C_2H_2Cl_4$ and phenol in the presence of an ammoniacal soln., the solvent is sepd. from the solute by fractional distn. *in vacuo* and the remaining solute is subjected to the action of steam and further vacuum distn. Fatty matter is dissolved from the distn. residue with petroleum ether

or other solvent, theobromine and tannin are dissolved from the residue with dil. alkali soln. and theobromine is pptd. from the soln. with CO_2.

Yeast-containing dentifrice. W. T. GREEN. U. S. 1,386,252, Aug. 2. Dentifrices are prepd. consisting largely of yeast; *e. g.*, a dry powder may be formed of yeast 150, pptd. Ca phosphate 300, saccharin 1.3, powdered ginger 20, 95% alc. 40, pancreatin 4, diastase 4, 85% H_3PO_4 4 and oil of peppermint 1.3 parts. Glycerol may be added to form a paste.

Embalming fluid. G. CALLODI. U. S. 1,386,157, Aug. 2. An embalming fluid is formed of NaCl 40 g., $CaSO_4$ 40 g. and turpentine 1 gal.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FREO C. ZEISBERG

The production of acid potassium sulfate from ammonium acid and potassium sulfates. W. DOMINIK. *Przemysl Chem.* 5, 10–5, 37–40, 63–7(1921).—The reaction between the NH_4HSO_4 and Na_2SO_4 or K_2SO_4, when fused in the presence of steam superheated to 200–400°, takes place according to the equation $M_2SO_4 + NH_4HSO_4 = 2MHSO_4 + NH_3$, for which K, equal to $\frac{[MHSO_4]^2}{[M_2SO_4].[NH_4HSO_4]}$, increases with the temp. according to a logarithmic function. When a mixt. of Na and K sulfates is used the const. is calcd. from the consts. of the component salts at the temp. in question. This calcn. depends also on the relative amts. of Na and K sulfates present in the mixt. The lack of steam in the gases coming into contact with the melt results in the production of pyrosulfates. It causes a more rapid evolution of NH_3 but decreases the viscosity of the melt. JOHN M. KRNO

U. S. Government air nitrate plant No. 2, Muscle Shoals, Ala. GEO. B. CRAMP. *Blast Furnace and Steel Plant* 9, 525–8(1921).—A non-technical, general and very elementary description of the plant. No quant. information is given. *By-product NH_3 recovery* from coke-oven gases is touched upon in the same manner. F. C. Z.

Causes of the burning through of a kettle used for the production of nitrite from nitrate by molten lead. ED. W. ALBRECHT. *Chem. Ztg.* 45, 726(1921); cf. A. Lottermoser *C. A.* 15, 3726.—A. has obtained excellent yields of nitrite, and a smoother and safer operation, by introducing the Pb in the form of thin sheets dipped in the molten nitrate. In this way there is less opportunity for the Pb to escape reaction by forming a layer at the bottom of the kettle. It is safer to take power from a special motor rather than from the main shaft of the factory, as in this way there is less chance of a temporary cessation of agitation, with the possible resulting mishap discussed by L. For the fusion kettle, cast iron is fully as satisfactory as cast steel. DONALD W. MACARDLE

The sulfur industry of to-day. HAROLD S. DAVIS. *Can. Chem. Met.* 5, 295–7 (1921). E. H.

Nitrogen products statistics. ANON. *Engineering* 112, 345–6(1921). E. H.

Arsenic, bismuth, selenium and tellurium in 1920. VICTOR C. HEIKES. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part 1, 51–72(preprint No. 7, published Sept. 22, 1921). E. H.

Fluorspar and cryolite in 1920. HUBERT W. DAVIS. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 65–80(preprint No. 9, published Sept. 1921). E. H.

Gypsum in 1920. RALPH W. STONE. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 55–64(preprint No. 8, published Aug. 31, 1921). E. H.

Sodium compounds in 1920. ROGER C. WELLS. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 123–34(preprint No. 14, published Sept. 30, 1921). E. H.

Strontium in 1920. GEORGE W. STOSE. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 93–5(preprint No. 12, published Sept. 17, 1921). E. H.

Graphite in 1920. L. M. BEACH. U. S. Geol. Survey, *Mineral Resources of U. S. 1920*, Part II, 81–6(preprint No. 10, published Sept. 16, 1921). E. H.

Helium in a sample of natural gas. J. E. G. HARRIS. *J. Inst. Petroleum Tech.* 7, No. 27, 14–16(1921).—A sample of natural gas from Hurghoda, Egypt, was examd. as follows: hydrocarbons were oxidized by repeatedly passing the sample over heated CuO, and the unattacked gases were collected over a 40% soln. of KOH. Decrease in corrected vol. ceased when 50 cc. of gas remained from an original sample of 2070 cc. The spectrum of this gas showed faintly the lines of He. The helium was sepd. from other gases by adsorbing them on charcoal at the temp. of boiling liquid air, and pumping off the He, as usual. The vol. of helium was estd. at 0.1 cc., corresponding to 0.005% in the original sample. W. F. FARAGHER

Introduction into the domain of pastes. FR. KIRCHDORFER. *Seifensieder-Ztg.* **48**, 598–9, 620–1, 639, 683–4(1921).—A general description is given of the types, properties and uses of org. substances employed for pastes, glues, cements, sizes, etc., together with some hints as to proper prepn. and correct use. The subject is treated from a general standpoint, general directions being given for waterproofing, preventing decompn. and obtaining normal concns. Applications are cited. P. ESCHER

The solution of the nitrogen problem (NAGANT) **15.**

Hydrocyanic acid. R. W. POINDEXTER. U. S. 1,387,170, Aug. 9. HCN is produced by heating natural gas or similar hydrocarbon material and injecting NH_3 into the material. The reaction may be carried out in a chamber filled with hot checker-work.

Synthesis of ammonia. C. BOSCH. U. S. 1,386,760, Aug. 9. A mixt. of H and N is repeatedly subjected to the action of a catalyst to form NH_3 with absorption of the NH_3 produced and addition of fresh mixt. between succeeding treatments.

Precipitating hydroxides with ammonia. M. BUCHNER. U. S. 1,386,920, Aug. 9. Hydroxides of metals such as Al and Zn which are substantially insol. in NH_3 soln. are formed by allowing NH_3 in an amt. which is several times the chem. equiv. of the metal present to act upon a salt of the metal, *e. g.*, $Al_2(SO_4)_3$ in the presence of H_2O. Cf. *C. A.* 15, 2342.

Upflow condenser for ammonia. N. H. HILLER. U. S. 1,385,827, July 26.

Cyanides or cyanamides. KARL PRINZ ZU LÖWENSTEIN and F. HAUFF. U. S., 1,386,941, Aug. 9. CH_4 is dissociated into H and C by heating and the pure C thus obtained is mixed with $BaCO_3$ or the like. The H is burned in air to obtain a mixt. of N and H_2O vapor. The N is caused to react with the mixt. of pure C and $BaCO_3$ or like material to form cyanide or cyanamide, at a temp. of 1200–1400°.

Lead arsenate. M. L. TOWER. U. S. 1,387,212, Aug. 9. Pb arsenate is made by dissolving PbO in dil. HOAc, adding arsenic acid in small streams and filtering off the pptd. Pb arsenate.

Lead arsenate. M. L. TOWER F. and L. BEGTRUP. U. S. 1,387,213, Aug. 9. In the manuf. of Pb arsenate from PbO and arsenic acid, the reaction is carried out in the presence of a neutral nitrate such as $Ca(NO_3)_2$ which serves to promote the reaction. Heavy grades of PbO may be used.

Potassium sulfate and aluminium oxide from alunite. J. L. SILSBEE. U. S. 1,386,031, Aug. 2. Alunite is crushed and roasted, treated with H_2O and mother liquor from a previous operation while hot to utilize the heat of the ore for dissolving as much K_2SO_4 as possible, and the liquor and suspended fines of Al oxide are sepd. from the ore

residue. The liquor is freed from fines of Al_2O_3 by a steam-heated thickener and is then cooled to permit crystn. of K_2SO_4.

Potassium chloride from feldspar or similar materials. J. ALLINGHAM. U. S. 1,386,486, Aug. 2. Minerals such as feldspar are heated with NaCl and S with limited supply of air so as to maintain reducing conditions, at a temp. of about 800-900°, and the reactioo products are lixiviated with H_2O and KCl is crystd. from the soln. thus obtained.

Treating phosphate rock. W. GLAESER. U. S. 1,387,151, Aug. 9. Phosphate rock is ground and heated to a temp. of about redness witb Na_2CO_3 and C, and the H_2O-sol. phosphate is leached out and treated with CO_2 in order to obtain Na_2HPO_4 and regenerate Na_2CO_3.

Recovering bromine from mixtures also containing chlorine. C. W. JONES. U. S. 1,386,117, Aug. 2. Br is recovered from mixts. also contg. Cl by treating the mixt. with sufficient alkali, *e. g.*, NaOH, to absorb tbe Cl and to absorb also 1 mol. of Br for each 5 mols. Cl, tbus converting the Cl into cbloride and forming a proportionate amt. of bromate. The bromate is sepd. from the chloride by fractional crystn. and the residual Br left after the absorption treatment is recovered, *e. g.*, by an absorbent.

Treating crude brines. H. H. DOW. U. S. 1,386,244, Aug. 2. Crude brines such as Mich. brines contg. mixts. of chlorides are freed from bromides and then from any Fe and Mo present by pptn., *e. g.*, by tbe action of NaOH in calcd. amt., and Mg is then pptd. with additional NaOH. Any NH_3 present is freed by the action of alkali and any alk. earth metal is then pptd. as hydroxide or carbonate to obtain a pure soln. of NaCl.

Catalyst for chemical synthesis. A. L. DAVIS and K. D. JACOB. U. S. 1,386,555, Aug. 2. A catalyst adapted for use io synthesis of NH_3 is prepd. by mixing solns. of $Fe(NO_3)_3$ and NH_4 molybdate, heating to the b. p., filtering, washing and drying the filtered out material, igniting and reducing the resulting product with a fluid such as H which is free from catalytic poisons.

Carbon-removing composition. G. D. HOOVER. U. S. 1,386,337, Aug. 2. A mixt. for removing C deposits from internal-combustion engines is formed of ether 2.5, alc. 3.5, C_6H_6 1 and NH_3 soln. 10 parts.

Removing carbon from internal combustion engines. G. TOROSSIAN. U. S. 1,386,385, Aug. 2. CCl_4 is admitted to an internal combustion engine while running under its own power to loosen C deposits and blow them out witb the exhaust.

Valve-grinding abrasive mixture. C. SHATTOCK. U. S. 1,386,432, Aug. 2. A mixt. adapted for use in grinding valves is formed of carborundum 1 lb., ground glass 4 oz., and 8 oz. of a soln. formed from lye 8 oz., grease 5 lbs. and H_2O 3 gals.

Heat insulation. A. K. BURGSTRESSER. U. S. 1,387,348, Aug. 9. A heat-insulating material adapted for covering pipes is formed of outer layers of asbestos fabric with an intermediate layer formed of infusorial earth and asbestos.

Insulating material. L. MCCULLOCH. U. S. 1,386,008, Aug. 2. An insulating material adapted for withstanding heating is formed of mica flakes bonded with H_3BO_3 and NH_4 borate mixed with bentonite clay and glycerol.

Composition for sealing metal cans. I. HOTSON-TAIT. U. S. 1,386,626, Aug. 9. A mixt. adapted for use in sealing metal cans cootg. perishable foods is formed of resin 6 oz., MeOH 6 oz., Fe carbonate 3 oz., flour paste 1 pint, molasses 7 oz. and HNO_3 2 drams.

Gelatinous composition for reproducing line documents. F. DORR. U. S. 1,386,996, Aug. 9. A material for the reproduction of line documents is formed of gelatin 100, $FeSO_4$ 1.5 parts and $BaSO_4$, kaolin or similar white substance which has no chem. action on the gelatin.

Cyanide furnace. R. M. MAJOR. U. S. 1,387,286, Aug. 9. The furnace is adapted for use with heated NaCN and NaCl mixts. It comprizes a refractory cyanide pot of Ni-Cr alloy and furnace for heating it, a hood for the pot which prevents cyanide from it from entering the furnace, and sep. flues for this hood and for the combustion products from the furnace.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Glimpses of Ohio ceramic industries. CHESTER H. JONES. *Chem. Met. Eng.* 25, 562–6, 619–22(1921). E. H.

Employment of aluminothermic corundum as a refractory product. ALBERT GRANGER. *Bull. official direction recherches sci. ind. inventions* 1921, 297–300.—Crude corundum was pulverized, washed, treated with H_2SO_4, first cold then hot, until no further action was observed. It was then further treated with HCl and thoroughly washed with water. Several formulas are given for prepg. mixts. to be fashioned into utensils for firing. Thus, corundum to pass a 150 sieve 8 parts, kaolin des Eyzies 1, argile de Berneçay 2. The mixt. is fashioned and fired. The product was found to withstand sudden changes in temp. and to bear the temp. of melted Pt without much fusion. L. W. RIGGS

Abrasive materials in 1919. L. M. BEACH AND A. T. COONS. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part II, 381–6 (preprint No. 29, published Sept. 16, 1921). E. H.

Material for preventing moisture accumulating on glass. M. C. PITTMAN. U. S. 1,386,362, Aug. 2. A prepn. for coating glass to prevent accumulation of moisture on its surface is formed of a pulp of cured tobacco leaves satd. with a mixt. of tobacco juice and glycerol.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

British Association Fuel Economy Committee fourth report. W. A. BONE, *et al. Gas J.* 155, 656–7(1921); cf. *C. A.* 14, 3144; 15, 1385.—Progress report. J. L. WILEY

Wilputte regenerative by-product coke oven. ANON. *Iron and Coal Trades Rev.* 103, 440–1(1921).—Description of the regenerative ovens for the Consett Iron Co. J. L. WILEY

A resumé of standard methods in sampling, analysis and classification of coal. A. TREVOR WILLIAMS. *J. Chem. Met. Soc. S. Africa* 22, 1–19(1921). E. H.

Further remarks on the origin of coal from lignin. FRANZ FISCHER AND HANS SCHRADER. Mülheim-Ruhr. *Brennstoff-Chem.* 2, 237–8(1921); cf. *C. A.* 15, 3548.—Polemical against Erdmann (*C. A.* 15, 3386). W. B. V.

Pulverized coal as a combustible. R. A. S. REDMAYNE. *Nature* 107, 812–4 (1921).—A review and discussion. W. H. ROSE

A new method for determining the volatile matter yielded by coals up to various temperatures. WILLIAM A. BONE AND LEONARD SILVER. *J. Chem. Soc.* 119, 1145–53 (1921).—The method involves carbonizing the coal in a silica tube heated in an elec. resistance-furnace, the former provided with a delivery tube and water seal for the exclusion of air. A charge of about 5 g. is weighed into a smaller silica tube closed at

one end and this is inserted and held in place in the retort tube which is inclined with the delivery end downwards. Heat is gradually applied, according to the character of the coal, up to temps. around 900°, which are measured by means of a thermo-couple and maintained const. until gas evolution ceases. Duplicate results show close agreement but are, as a rule, lower than those obtained by the so-called "American" and "Crucible" methods. The authors claim the following advantages over the methods referred to above: (1) accurate knowledge of temp. and ease of regulating it; (2) good control of rate of heating; (3) prevention of oxidation through the use of an inert atmosphere; (4) completeness of carbonization at a given temp. since heating is continued until evolution of gas stops; (5) possibility of collecting the gases evolved for examn.; and (6) the shaping of the coke in a cylindrical form convenient for subsequent testing.

H. L. Olin

The conversion of coal to oil by means of hydrogenation. II. Hydrogenation of coal by means of carbon monoxide. Franz Fischer and Hans Schrader. Mülheim-Ruhr. *Brennstoff-Chem.* 2, 257–61(1921); cf. *C. A.* 15, 3193.—CO may be regarded as a hydrogenating agent in the presence of H_2O vapor at 400°, provided the gaseous equil. can be estahlished rapidly enough by the aid of a catalyst. At atm. pressure, however, there is no appreciable reaction; at 130–140 atm., maintained for 3 hrs., the Et_2O-sol. fraction of the reaction product from Rhenish lignite rose from the 7% yield in presence of an inert gas, to 30%. H_2 in the presence of the same amt. of water yielded about 12%. In both cases the residue also became more sol. in C_5H_5N. Bituminous half-coke gave little evidence of hydrogenation after similar treatment with either CO or H_2, and lignite half-coke was only slightly affected hy H_2, hut CO gave a 22% yield of Et_2O-sol. A Lohberg gas-coal gave 13% with CO and 10.5% with H_2. Raising the pressure increases the yield slowly; *e. g.* the Et_2O-sol. from Rhenish lignite increases from 22% at 50 atm. to 30% at 140 atm. Increasing the temp. has a similar effect up to the temp. at which the products begin to undergo decompn., about 450°. About 400° it is also difficult to make the app. tight at these high pressures. At 300° the yield of ext. drops to 9%. It was thought that the iron walls of the app. catalyzed the production of the relatively inactive mol. H_2, and that a copper container would give higher yields, but this expectation was not realized. When the quantity of water present was varied from 10 cc. to 20 and 40 cc. for 15.8 g. of coal the yield of Et_2O-ext. rose from 14% to 30% and 35%. In all the cases the ext. was a red-brown salve which on distn. gave about 15% of a light oil, 40% of a yellow buttery mass and 12% of a dark brown soft pitch, leaving a residue of 32% of a dark resin. The max. yields from the CO process and those from the NaCOOH process previously described are, resp.: Bituminous half-coke 0.6%, 10%; gas-coal 13, 39%; lignite half-coke 22, 32%; Rhenish lignite 35, 45%.

W. B. V.

Fuel briquets in 1920. W. F. McKenney. U. S. Geol Survey, *Mineral Resources of U. S., 1920*, Part II, 89–91 (preprint No. 11, published Sept. 19, 1921).

E. H.

Peat in 1920. K. W. Cottrell. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 41–3 (preprint No. 6, published Sept. 7, 1921).

E. H.

A new method for gasifying coal dust. K. M. Balley. *Chem.-Ztg.* 45, 789–90 (1921).—The essentials of this method involve (1) a generator in which coke is maintained at a temp. of 1400–1600°, (2) a bunker supplying coal dust, and (3) a source of superheated steam. The steam is admitted to the generator together with coal, which immediately begins to undergo destructive distn. A part of the coke formed reacts with the steam to form water gas; the remainder serves to maintain the supply for packing the generator. The mixt. of water gas and distn. products goes through another generator, maintained at 1400° to gasify any tar present, and is then cooled, filtered and

stored. A certain coal with a heat value of 7,650 Cal. per kg. yielded 1.65 cu. m. of gas with a value of 4100 Cal. per cu. m. H. L. OLIN

Report of the forty-fourth meeting of the Société technique du gaz en France. President's address. EDOUARD KAHUFFER. *J. usines a gaz* **45**, 257–65 (1921).—K. reviews the part played by the gas industry during the war. An app. of the tensimeter type is described for the rapid detn. of the vapor tension of *benzene* in wash oil corresponding to the % of benzene. The U tube is filled with Hg by means of a leveling flask and the shorter limb tightly closed by a stopper. Const. temp. is maintained by means of a water jacket. After the air is driven out, the Hg column is depressed and the space filled with the oil to be tested. The barometric level of the Hg is read off, the vapor pressure of water deducted, and the vapor pressure of the benzene detd.; from this is deduced the % of benzene in the oil by aid of a curve. It is found that for each % of benzene, the vapor pressure increases 2 mm. up to 5% of benzene. This detn. allows for const. control of the washing process. J. L. WILEY

The calculation of the efficiency of complete gasification. H. STRACHE AND A. GROSS. Vienna. *Braunkohle* 1921, No. 42–3; see *C. A.* **15**, 2171. C. C. DAVIS

A nomographic chart for gases. T. B. MORLEY. *Engineering* **112**, 302–4(1921).—Charts for detg. directly the principal properties of gases in internal-combustion engines *viz.*, pressure, volume, temperature, intrinsic and total energy and adiabatic changes, are described. H. L. OLIN

Pressure-volume deviation of methane, ethane, propane and carbon dioxide at elevated pressures. G. A. BURRELL AND G. W. JONES. Bur. Mines, *Repts. of Investigations* No. 2276, 6 pp. (1921).—The methods of prepn. of the gases and the original data (not previously published) of Burrell and Rohertson (*C. A.* **10**, 1589; **12**, 758) are given. E. H.

What goes on in a water-gas machine. M. E. BENESH. Am. Gas. Assoc. *Am. Gas J.* **115**, 275–8, 283–4(1921); 1 diagram, 6 charts; cf. Harper, *C. A.* **13**, 1383; Clement, *C. A.* **6**, 800.—B. discusses the problem of distribution of heat in a water-gas machine and control of fuel-bed temp. By detg. the % of undecomposed steam in the blue gas, variations in the operation could he avoided and a real index of conditions be realized. *The Water Gas Indicator* has been devized for recording and indicating continuously the production and fuel-bed condition of a carbureted-water-gas machine by giving directly the % of steam decomposed by the fuel bed. The underlying principle of the method is that of the familiar wet-hulh thermometer used for atm. humidity detns. graduated in % decompn. of steam. The detn. is made on the partially decomposed steam leaving the generator to the carburetor, and is sufficiently accurate for practical purposes. Exemplary detns. are given. Also in *Gas Age-Record* **48**, 559–63 (1821). J. L. WILEY

Water-gas production with recovery of tar and ammonia. A. SANDER. Darmstadt. *Brennstoff-Chem.* **2**, 261–4(1921).—A description of the double-gas and tri-gas processes as practiced by the *A.-G. für restlose Vergasung*, of Frankfort a. M. W. B. V.

Modern methods of by-product coking in the lower Rhine-Westphalian mining regions. BRUNO SIMMERSBACH. *Chem.-Ztg.* **45**, 673–6, 723–6(1921).—Methods of obtaining NH_4 salts from coke-oven gas and of distg. coal tar are discussed in some detail. The paper is replete with statistical tables indicating the output of coal, tar, coke, and by-products from the regions mentioned. DONALD W. MACARDLE

The development of foreign low-temperature coking on a large scale. A. THAU. Gelsenkirchen. *Brennstoff-Chem.* **2**, 225–9, 244–51, 264–7(1921).—A detailed description, with sketches and photographs, of the Greene-Laucks, Coalite and Carbocoal processes, with some data on thermal performance and yield and character of the prod-

ucts. The development of a steel or cast iron which will not gradually change in dimensions when held for a long time at 550° is mentioned as one of the outstanding problems. W. B. V.

Preparation of viscous lubricating oils from coal tar (SCHREIBER) 13. Present availability of oil shale (WEBB) 22. Gas and other products from petroleum pitch (U. S. pat. 1,386,945) 22.

Fuel from lignitic coal. C. H. URQUHART. U. S. 1,386,473, Aug. 2. Fuel is prepd. in original mine-run lump form by fusing lignitic coal with a binder such as melted pitch which serves to form a compact fuel on heating to a carbonizing temp.

Preparing low grade coal for fuel. C. H. URQUHART. U. S. 1,386,472, Aug. 2. Low grade coal is heated until cracks open up in it, the cracks are filled with melted pitch or similar binder and the coal and binder are then heated sufficiently to cause carbonization.

Recovery of nitrogen compounds during dry distillation. W. OSTWALD. U. S. 1,386,723, Aug. 9. In coking coal or other similar material, a chloride such as an alk. earth metal chloride is mixed with the fuel and the mixt. is heated in a closed chamber to which steam (but no air) is supplied. NH_4Cl is thus formed and is recovered.

Combined coal- and water-gas generator. W. D. WILCOX. U. S. 1,386,825, Aug. 9. The app. is adapted for the production of gas for domestic use. Blast gases produced during the blast period in a water-gas generator are utilized in the extraneous heating of coal in a sep. coking chamber, and at the same time water-gas is passed through the coal economically to produce a combined coal- and water-gas. Heat from the blast gases is also utilized for the production of steam during the subsequent run period.

Oil-gas producer. E. A. WEST and E. E. PARSONS. U. S. 1,386,038, Aug. 2.

Ammonium chloride. E. PIRON. U. S. 1,386,278, Aug. 2. The temp. of coke-oven gases is reduced without the addition of H_2O to about the dew point and the gases are then washed with aq. liquor to absorb the NH_4Cl which they contain.

Horizontal coking oven. O. PIETTE. U. S. 1,386,799, Aug. 9. The pat. relates to the arrangement of the regenerators and other structural features.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Procedure and products of petroleum refining. C. K. FRANCIS. *Chem. Age* (N. Y. 29, 271–3(1921).—A popular description of the processes and products (brief) of refining in the Mid-continent field. W. F. FARAGHER

Viscosity-temperature curves of fractions of typical American crude oils. E. W. DEAN AND F. W. LANE. *J. Ind. Eng. Chem.* 13, 779–86(1921).—Fractions obtained from 3 crude oils, typical of the 3 general types of petroleum, by the Bureau of Mines procedure for analyzing crudes, and some mixts. of these fractions, were examd. A special set of Ostwald-type viscosimeters was used, the temps. being maintained by the usual form of thermostat. Selected temps. between 0° and 100° were chosen for each sample. Numerous tables and graphs give the data obtained. Variation of viscosity with temp. is least with fractions from a paraffin-base crude, and greatest for those from an asphalt-base crude. Variations for a mixed-base product are intermediate, but closer to the former than to the latter. There seems to be no simple rule by means of which the variations can be predicted. Viscosity-temp. curves can be represented by an equation of the general form: $V_t = 1/(K + At + Bt^2)$. The consts. for a given oil can be calcd. from the kinematic viscosities (V_t) dtd. at 3 temps., the use of the method of least squares not being necessary. W. F. FARAGHER

Methods for reclaiming B. S. C. V. FORNES. *Petroleum Age* 8, No. 10, 33–4 (1921).—The chem. and the mechanical methods for the treatment of B. S. (bottom settlings) are described. By using the chem. and mechanical processes jointly, the efficiency of the plant may be increased by as much as 40%, while the cost is about the same as that of either of the 2 processes separately. R. L. SIBLEY

Common characteristics of crude petroleum emulsions. E. E. AYRES. *Petroleum World* 18, 406–7(1921).—Crude oil emulsions as they occur industrially show an unexpected sameness. In order to increase the rate at which the more stable of these emulsions can be sepd., the H_2O particles should be caused to unite to form larger single globules. One method is to add to the emulsion a small amt. of a material sol. in petroleum but contg. a substance classified as a "water-sol. protective colloid." Such a substance is starch, which, normally insol. in oil, can be combined with intermediate substances in such a way as to become apparently sol. in oil. R. L. SIBLEY

Electrical processes for the dehydration of crude petroleum emulsions. ANON. *Petroleum World* 18, 401–6(1921).—A large % of emulsions that will not yield to heat below the b. p., applied even for an extended time, yield readily to the elec. process. The distg. process of dehydration is wasteful in fuel consumption and involves high charges for upkeep and labor. A saving of 50 to 90% in favor of the elec. process results from these items alone. The elec. treatment does not crack the oil but conserves to a high degree the lighter volatiles. The H_2O taken out by the elec. method is entirely free from emulsion or oil. Plants handling emulsions varying in gr. from 11 to 35° Bé. and a H_2O content as high as 85% have shown by distn. tests that the cleaned oil often contains as little as 0.5% H_2O. The total cost of treatment is 1–3 c. per barrel of net oil. R. L. SIBLEY

Heat test of oil. C. V. STRATFORD. *J. Soc. Automotive Eng.* 9, 280–1(1921).—Finished engine oils are put in a small nickel-plated cup about 1.5 in. in diam. and 1.5 in. high and filled to within about 0.25 in. of the top. The cups are heated on a hot plate to 550° F. and held there for 10 min. and then allowed to cool. There is an incrustation on the inside of the cup immediately above the surface of the oil which is rather soft and carbonaceous regardless of whether the test is made on paraffin- or asphalt-base oils. There is also a formation of a gum or resin on the outside of the cup due to creeping over the top of the cup and oxidation to form a gum or resin. The appearance of the deposit and the fact that a poor oil always leaves a sediment when poured out of the cup, while a good oil will not, enables one to det. if the sample used is a good engine oil. R. L. SIBLEY

Manufacture of natural gasoline. ANON. *Oil and Gas J.* 20, No. 19, 74–80 (1921).—A description and discussion of the compression, absorption and refrigeration processes of manufacturing natural (casinghead) gasoline. R. L. SIBLEY

The absorption of gasoline from casing-head gas by activated charcoal. H. R. AUKERSWALD. *Mech. Eng.* 43, 601–2, 606(1921).—A. gives diagrams of the app. and description of the method used for comparing the charcoal adsorption with compression plant practice on a rich casinghead gas from the Drumright (Okla.) field (2.5 gal. per M cu. ft.). Charcoal will adsorb all of the gasoline at atm. pressure if the rate of passing the gas, and the percent of satn. of the charcoal are controlled (9–12 ft./sec. through the absorber, and 15.3% by vol. of gasoline). At the correct velocity, the charcoal adsorbs 22.5% by vol. or 25.3% by wt. of gasoline. It is not possible to distil with superheated steam or direct heat and then condense all of the vapors adsorbed, at the pressures and temps. ordinarily employed in compression plants. Even if all of the vapor could be condensed, it is not practical to use the charcoal process on such a rich gas if it is necessary to return to the lease as much as 65% of the discharged gas. Smaller yields are indicated by a charcoal adsorption followed by lab. distn. with glycerol

than by the usual physical testing equipment used in the field. The fuel requirements are larger than for a compression plant with rich casinghead gas, and greater in the case of a leaner gas than for a low-pressure absorption plant. Cooling of the absorber would have to be effected with some other medium than the residual gas, unless it were recirculated several times after cooling in coils. W. F. FARAGHER

Testing motor fuel benzene. GANSWINDT. *Export-Anzeiger* 21, No. 17, 1(1921).—A simple method for distinguisbing sharply between aliphatic and aromatic hydrocarbons is the *Dracorubin* metbod of Dietrich. Tbe basis of it is purified dragon-blood which does not dissolve in aliphatic but does dissolve with blood-red color in aromatic bydrocarbons, in alcobol and in halogen derivs. of the paraffin hydrocarbons. If a test paper soaked in an alc. soln. of dragon-blood is dipped into tbe liquid to be tested, the latter will remain colorless if it is benzene, but becomes crimson if benzene or benzene-spirit is present. To distinguish the latter two, 1–2 cc. are shaken thoroughly in a test-tube witb a drop of water; if the latter dissolves clearly in tbe liquid, this consists of benzene-spirit, as water does not dissolve in pure benzene but gives a turbid mixt. J. L. WILEY

Notes on the oil-shale industry with particular reference to the Rocky Mountain district. M. J. GAVIN, H. H. HILL AND W. E. PERDEW. Bur. Mines, *Repts. Investigations* No. 2256, 35 pp.(1921).—A short paper giving a general discussion of the subject and a comprehensive list of references. The descriptive part of the paper is compiled from published articles and books for those who are interested only in a general discussion of the subject. W. F. FARAGHER

Present availability of oil shale. FRANCIS P. WEBB. *Am. Gas J.* 115, 271–2 (1921).—The Index Shale Oil Co.'s *retort* is described. It is a horizontal, tubular retort with positive feed, but witb no moving interior parts. The capital cost is far below that of other types and does not exceed $350 per day ton. It has the highest throughput known, tbe greatest flexibility at all stages, and perfect heat control allowing of great variations in range of distn. The residue can be delivered in powdered form, calcined or with fixed amts. of hydrocarbon. It can be applied to *coal distn.* with recovery of by-products. J. L. WILEY

The Colorado-Utah petro-shales. J. B. BENSON. *Petroleum Times* 6, 469–70 (1921).—B. proposes the use of the following terms in place of the inaccurate and misleading expressions now in use: *petrogen* for that material which through destructo-constructive distn. produces petroleums; *petro-shales* are shales still in their primary unaltered condition contg. petrogen but not petroleum; oil shales were originally petro-shales which througb later earth heat have given up their petrogen and then through absorption have taken up the resultant petroleum; *shalene* is a term used to distinguish the product from shales which correspond to the gasoline fraction. Petro-shales are spoken of as massive and paper shales. The latter consists of much thinner beddings or measures than tbe massive. Between each bedding is a thin layer of argillaceous material contg. no pretrogen and this, on weathering, decomposes and permits the petroliferous beddings to sep. As a rule the massive variety is of a slightly higher grade than the paper, although wben the ledge is penetrated beyond the weathering, the paper shale becomes solid and the oil yield usually increases. R. L. SIBLEY

The thermal decomposition of shales. I. Heat effects. RALPH H. MCKEE AND E. E. LYDER. *J. Ind. Eng. Chem.* 13, 613–8(1921).—The origin, nomenclature, classification and distribution of shales and field observations on shale deposits are discussed briefly. An app. and method for measuring the initial temp. of decompn. of shales upon retorting, are described. Pyrobitumens do not decompose to form "petroleum oils" as primary products, but yield first a heavy solid or semi-solid bitumen. The formation of this primary product occurs at a sharp temp. interval (400–410°)

for the shale used (Parachute Creek, near Grand River, Colo.). A *bibliography* is appended. II. Determination of the heat of reaction involved in their decomposition. *Ibid* 678–84.—A method and an app. for detg. the heat of decompn. of oil-shales are described. The *coeff. of thermal cond.* (c. g. s. units) of shale is 0.00086. The *sp. heat* of shales averages 0.265. The conversion of the kerogen of oil-shale to oil (to the primary pyrobitumen mentioned above, rather than to the shale-oil of the usual destructive distn. W. F. F.) required 421–484 cal. per g. of oil and gas produced for the 3 samples of shale used. A *bibliography* is appended. W. F. FARAGHER

Removing wax from cylinder stock. EARL PETTY. *Oil and Gas J.* 20, No. 19, 89(1921).—Cylinder stock, which is the residue obtained from overhead distn. of light crude, contains such a high wax content that it solidifies at about 85° F.. By redesigning the bowl of a centrifugal separator, advantage has been taken of the fact that a blending naphtha can be used that will give a wax naphtha soln. and an oil or bright stock soln. at a temp. of 0° to −10° F. which can be discharged from the bowl as two fluid components: a wax naphtha stream as the heavy compoeent and a bright stock naphtha stream as the light component. This last can be used for high-grade motor lubricants. R. L. SIBLEY

Method of packing samples of asphalt. J. KEWLEY. *J. Inst. Petroleum Tech.* 7, No. 27, 14(1921).—Ordinary tin boxes, the insides of which are amalgamated, are used, since asphalt does not adhere to this surface. W. F. FARAGHER

Origin and composition of certain oil shales (THIESSEN) 8. Electrically heated still (for petroleum) (U. S. pat. 1,386,484) 1.

Cracking petroleum oils. D. E. DAY. U. S. 1,386,768, Aug. 9. Low-boiling hydrocarbons are formed from hydrocarbons of higher h. p., by passing the high boiling material into a zone contg. cast Fe, fireclay or similar spreading material which is heated to a cracking temp., causing production of low boiling products and deposition of C. The low boiling material is led off and condensed and the supply of fresh material to the zone is intermittently interrupted and the C deposited is burned away. During the latter operation the cracking process is continued in an adjacent chamber filled with spreading material and heated from the zone in which the C is being burned away. The two chambers may be positioned one within the other.

Distilling mineral oils. E. A. RUDIGIER. U. S. 1,386,077, Aug. 2. H_2O is removed from mineral oils by passing the oil at atm. temp. on to an exteoded surface such as an open pan located in the vapor space of a still, which contains oil undergoing distn. and permitting the oil to flow over the surface and thence into the main body of oil being distd., the vapors being led off and condensed.

Fractional distillation. V. T. GILCHRIST. U. S. 1,386,467, Aug. 2. In the fractional distn. of petroleum hydrocarbons or similar materials, vapor is sepd. at certain temps. as it passes through the app. used, to obtain condensates, and each successive condensate is fractionally distd. by the heat of the vapor previously sepd. from it, and additional condensate and sepd. vapor are similarly handled to effect further sepn. An app. is described.

Gas and other products from petroleum pitch. K. NOMI. U. S. 1,386,945, Aug. 9. Coke, volatile oil and gas contg. H are obtained by heating petroleum pitch in a retort to a temp. of 500–600° and collecting the products, distg. the volatile oil obtained and mixing its heavier fraction with additional petroleum pitch, heating the mixt. to 500–600° and collecting the products.

Asphalt. H. R. WARDELL. U. S. 1,385,511, July 26. A mixed-base petroleum residuum is mixed with an asphaltic-base petroleum residuum and the mixt. is heated

to a temp. above that required for complete expulsion of H_2O vapor but below that of destructive distn. while blasted with air to obtain an asphalt which is solid at ordinary temp.

Dense absorbent charcoal. L. F. HAWLEY. U. S. 1,385,826, July 26. Charcoal having a sp. gr. of 0.95 or higher and suited for absorbing gases is made by forming blocks from comminuted wood under a pressure of at least 30,000 lbs. per sq. in. and then distg. the blocks under a maintained mechanical pressure of at least 100 lbs. per sq. in. Cf. *C. A.* 15, 1396.

Retort for destructive distillation of wood or similar materials. E. E. QUINKER. U. S. 1,385,470, July 26. The retort is formed of a horizontally placed drum of metal plates with its bottom supported on a masonry foundation and its sides exposed to heat from combustion gases but protected from direct contact with the hot gases by replaceable shield plates of heavy metal.

23—CELLULOSE AND PAPER

A. D. LITTLE

Chemistry in paper-making. J. L. A. MACDONALD. *Chem. Trade J.* 69, 397–9 (1921). E. H.

French dyes for coloring paper. LHOMME AND ARGY. *Papeterie* 43, 511–4, 554, 692–9, 782–6(1921).—A list is given of a number of colors put out by the "Compagnie Nationale de Matières Colorantes et de Produits Chimiques" for the coloring of paper, with the corresponding names under which the most important German firms put out the same or similar colors. A. P.-C.

Cellulose from straw, jute or similar vegetable materials. C. A. BRAUN. U. S. 1,387,441, Aug. 9. Vegetable material such as jute, straw or nettles is heated with an aq. soln. of Na_2SO_3 and Na_2S or Na_2CO_3 and Na_2S in order to obtain cellulose adapted for paper manuf.

Cellulose from fibrous material. H. GEVERS. U. S. 1,385,744, July 26. In the production of cellulose from wood chips or similar fibrous materials, a digestion liquor (which may be formed of soda or sulfate soln.) is preheated, introduced into a digester charged with fresh material and the digestion is continued with heat supplied by steam from the preheating of a succeeding batch of digestion liquor.

Cellulose acetate composition. W. G. LINDSAY. U. S. 1,386,575, Aug. 2. A mixt. of cellulose acetate and tricresyl phosphate together with a solvent of both, *e. g.*, acetone, is used for the manuf. of sheets or other articles. Urea and dichlorohydrin may be added to the compn.

Threads, films or sheets from viscose. M. MÜLLER. U. S. 1,386,521, Aug. 2. Artificial threads or other forms are made from viscose by squirting the viscose into a pptg. bath contg. acidified waste lye of sulfite cellulose.

Waterproofing paper or similar materials. L. HEILBRONNER. U. S. 1,387,004, Aug. 9. A supple waterproofing is formed on paper or other fabric by treating the fabric with a soln. of gelatin and agar-agar contg. $K_2Cr_2O_7$ and $CaCl_2$ or glycerol and $(NH_4)_2CO_3$ and, after drying, treating the impregnated fabric with oil. Cf. *C. A.* 14, 2867.

Composition for waterproofing paper or other porous materials. W. V. LANDER. U. S. 1,386,711, Aug. 9. A mixt. adapted for filling the pores of paper, leather-board or the like is formed of crude petrolatum and rosin dissolved in gasoline.

Treating clay for coating paper. J. H. RYAN. U. S. 1,385,716, July 26. Small lumps of clay are heated to dry them and effect a preliminary oxidation, mixed with H_2O to settle out any grit, treated with NH_4OH to neutralize acid and the pulp is then

thoroughly ground in a pebble mill. It is then treated with a small amt. of a bleaching agent such as Na_2O_2 or oxalic acid and the grinding of the mixt. is continued for 2 hrs. after which it is withdrawn from the mill, washed out with H_2O by decantation and filtering and subjected to a drying action to obtain material adapted for easy disintegration in the manuf. of coatings for paper.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Biographical note on Auguste Rosenstiehl. MAURICE PRUD'HOMME. *Bull. soc. ind. Mulhouse* 86, 159–72(1920). E. H.

Salient points in the dyeing and finishing of velours. GEORGE E. TEMPLETON. *Am. Dyestuff Rep.* 9, No. 10, Tech. Sec. 36–7(1921).—There are many grades of velours on the market, some of which should not be classed as velours. Details of the manuf. of velour are described. Dyeing should be at a temp. not higher than 52°. Acid dyes are preferred though chrome colors may be used. After dyeing the goods should be examd. over a rough perch to det. if they have been properly dyed. The pieces are then renapped just enough to raise the previous nap and sheared. After shearing the goods are steamed, pressed lightly, resteamed, and allowed to condition in a damp cool room. L. W. RIGGS

Causes of cloudy and shafy effects in worsted piece dyes. KARL R. MOORE. *Am. Dyestuff Rep.* 9, No. 10, Tech. Sec. 37–9(1921).—Worsted fiber is easily affected by heat and cold, alkalies and acids. Unskilled handling and lack of uniformity in the application and removal of chemicals and other foreign matter will have a pronounced effect on the fiber. Incomplete emulsification and subsequent removal of spinning oils will cause clouds to appear in the dyed goods. Soaps for scouring should be made from olive foots stocks or saponified red oil. Streaky effects are caused by the incomplete removal of the warp size and are always accompanied by a two-color effect. Potato starch sizing should be avoided on account of the difficulty with which it is removed. Inefficient crabbing or decatizing will result in a listed effect after dyeing. Many other details are given for avoiding uneven dyeing. L. W. RIGGS

Control of bleach-house processes. H. W. EASTMAN. *Am. Dyestuff Rep.* 9, No. 10, Tech. Sec., 39–40(1921).—It is the custom to control the concn. of the sour liquor by means of the Twaddell hydrometer, which registers sp. gr. If the goods are insufficiently washed following the bleaching operation, the salts of Ca and Na will be introduced into the sour liquor and change the gravity so that the hydrometer no longer indicated true acid concn. The acidity should be controlled by titration with *N* NaOH with phenolphthalein indicator. A control table is arranged to show the cc. of *N* NaOH required to neutralize the acid in 100 cc. of tank liquor, also the number of lbs. of H_2SO_4 to add to restore the sour bath to a concn. representing 1° Tw. in various sized tanks. The directions may be followed by a person with no knowledge of chemistry. L. W. RIGGS

Alkali fusions. III. Fusion of phenylglycine-*o*-carboxylic acid for the production of indigo (PHILLIPS) 10. Dyes derived from phenanthraquinone (WATSON, DUTT) 10. Halogenated nitrobenzaldehydes and halogenated indigos (JANSE) 10. French dyes for coloring paper (LHOMME, ARGY) 23.

Speck-dye composition. O. L. PETERSON. U. S. 1,386,201, Aug. 2. A compn. for speck-dyeing is formed of NaCl 4.6, $CuSO_4$ 3, tartar emetic 1, H_2O 27.7, and hematin paste 55.4 parts.

Waterproofing textiles, etc. W. ALEXANDER. U. S. 1,385,854, July 26. Textile fabrics or other permeable materials are waterproofed by successive treatment with an aq. soln. and suspension of Na stearate and $Al_2(OH)_6$ and $Al_2(SO_4)_3$ soln., with an intermediate drying.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

The analysis of white paints. M. LOMBARD. Lab. Municipal de Paris. *Ann. fals.* 14, 261–8(1921).—For the analysis of white pigments which may contain one or more of ZnO, ZnS, $CaCO_3$, $CaSO_4$, $PbCO_3$, $PbSO_4$, $BaSO_4$: *A*. One g. or more of the pigment is treated with 25–30 cc. of 10% $(NH_4)_2CO_3$ and 10 cc. of NH_4OH, warmed on the H_2O-bath, decanted through a filter, treated again twice with about 15 cc. of $(NH_4)_2CO_3$ and NH_4OH, and finally washed with H_2O contg. a little NH_4OH. If $CaSO_4$ is present the time of each treatment should be at least ½ hr. The filtrate is evapd. to half its vol. on the H_2O-bath to remove part of the NH_4 salts, acidified with HCl in the presence of litmus, brought to boiling, 5 g. of Na phosphate (dissolved in a little H_2O) are added, and the liquor is made distinctly alk. to litmus with NH_4OH. It is boiled until the ppt. is cryst., filtered on a tared gooch, washed with hot H_2O, dried at 100° and weighed as $ZnNH_4PO_4$, and then ignited and weighed as $Zn_2P_2O_7$ so as to check the purity of the ppt. SO_3 is detd. in the filtrate by pptg. with $BaCl_2$. Owing to the large amt. of phosphates and of NH_4 salts, the clear liquid is decanted from the ppt. through a filter, and the ppt. is then boiled with a few cc. of dil. HCl. It is then transferred to the filter, washed, ignited, and weighed. *B*. One g. of powder is treated with 30–40 cc. of a mixt. contg. at least 25% alc. and 10% AcOH, warmed gently on the H_2O-bath, decanted through a filter, treated 2 or 3 times again with a little less of the mixt., and washed with a mixt. of alc. and H_2O. The combined filtrate and washings are evapd. to drive off the alc., dild. somewhat if too concd., a slight excess of $K_2Cr_2O_7$ is added, allowed to stand for a few hrs. in a warm place, filtered through a gooch, dried at 100° to const. wt., and calcd. to $PbCO_3$ or to white lead. The filtrate is made strongly alk. with NH_4OH, and CaO is detd. by pptn. with $(NH_4)_2C_2O_4$ as usual. If desired, ZnO can be detd. in the filtrate by boiling off part of the NH_4OH, acidifying with HCl, and proceeding as above for ZnO. The method is not applicable if both $CaSO_4$ and $PbCO_3$ are present, owing to the formation of $PbSO_4$ and $CaCO_3$. *C*. One g. of pigment is treated with 10 cc. HNO_3, evapd. almost to dryness to drive off excess of HNO_3, and the residue is taken up with $(NH_4)_2CO_3$ and NH_4OH and treated as in *A*. The ZnO is detd. in the filtrate as above, the difference between the two Zn detns. being calcd. to ZnS. The residue from the $(NH_4)_2CO_3$ treatment is digested with sufficient 10% HNO_3 to dissolve the carbonates formed, filtered through the same filter, washed, ignited, and weighed, giving $BaSO_4$. In the filtrate Pb and CaO are detd. and calcd. to $PbCO_3$ and $CaCO_3$, resp. Results are given for both known mixts. and com. pigments, the latter totalling 98.42–99.53%. In the presence of $CaCO_3$ and $CaSO_4$ or $PbCO_3$ the results for ZnS are slightly low. The results for total Pb are accurate. The results for total CaO are accurate in the absence of Pb, but somewhat high if the latter is present. The results for $BaSO_4$ are slightly low; but this is really due to the presence of impurities in the $BaSO_4$, provided proper precautions are taken for the detn. If $BaCO_3$ and ZnS are present, on treating with HNO_3 $BaSO_4$ is formed, and the original $BaSO_4$ must be detd. in a sep. sample by treating with HCl. It is claimed this procedure is sufficiently accurate for most cases, and is probably as accurate as more complicated ones. A. P.-C.

White lead in painting. ANON. *Engineering* 112, 323–4(1921); *La Ceruse,*

p. 64–9(1921).—A presentation of arguments, mostly economic, against the proposal of the International Labor Conference to prohibit the use of white lead in paint. Many so-called cases of Pb poisoning are wrongly diagnosed; there is no effective total substitute for white lead; the chief danger of poisoning is due to dust, and to carelessness on the part of the workmen, etc. F. A. WERTZ

Practical hints to varnish makers. W. W. KING. *Paint, Oil and Chem. Rev.* **72**, No. 10, 10–11(1921).—A lecture. Coal-tar solvents may often be used to advantage in thinning varnish bases; small scale expts. indicate that electrically heated varnish kettles are economical in operation; "cumar" (coumarone resin) has qualities which recommend its use in varnishes. F. A. WERTZ

Iron oxide pigments. RUSSELL S. PENNIMAN, JR. *Paint, Oil and Chem. Rev.* **72**, No. 10, 9, 21–2(1921).—A review, especially of the manuf. and uses of artificial hydrated yellow oxides of Fe. (Cf. U. S. pat. 1,327,061, *C. A.* **14**, 804.) F. A. WERTZ

Light-proof lithopone. STEINAU. *Chem. Ztg.* **45**, 741–2(1921).—The gray coloration of lithopone on exposure to light and moist air takes place most readily when Cl compds. such as traces of $ZnCl_2$ are present; this appears to be due to a slow dissociation (cf. *C. A.* **9**, 968). Calcining the pptd. lithopone *in vacuo* or in reducing or inert gases favorably affects light-proofness, but such a process is not commercially applicable. The possibilities of making light-proof lithopone depend either on the total exclusion of Cl, or a modified manufg. process in the presence of Cl. The purification of the Zn soln. by pptn. with $CaCl_2$ gives bulky, worthless ppts. of $CaSO_4$, $Fe(OH)_3$, Mn_3O_4, etc., and the process requires expensive filtering, is injurious to the health of the workmen, and is liable to cause dangerous explosions. By a process of the author's (no suggestion of the method is given), the use of Cl compds. is entirely eliminated, the ppts. are small in vol. and consist of pure Fe hydroxide and Mn_3O_4, which have commercial value, filtration costs are reduced, and there is only a very small loss of Zn salts. The product is very white and light-proof. F. A. WERTZ

Lac and shellac. H. A. F. LINDSAY AND C. M. HARLOW. *Indian Forest Records* **8**, I, 162 pp.(1921); *J. Soc. Chem. Ind.* **40**, 306–7R(1921).—A report by the Indian Govt. gives complete details of the shellac industry; suggests the establishment of "brood farms" for the production and distribution of brood lac; the cultivation of "host trees" which produce the better qualities of shellac; the establishment of a research organization; publication of reliable crop forecasts, etc. F. A. WERTZ

The bleaching of shellac. S. T. GADRE. *J. Indian Industries and Labor; Chem. News* **123**, 127–8(1921).—For bleaching shellac, add 5.5 lbs. of the shellac to 3 gal. boiling H_2O contg. 1 lb. Na_2CO_3; and to this add a filtered soln. of 5.5 lbs. bleaching powder and 4.5 lbs. Na_2CO_3 in 10 gal. H_2O. The lac dye bleaches very quickly, but the destruction of the yellow color of the erythrolaccin is much slower. On exposure to air and light, bleached shellac rapidly undergoes a change into an alc.-insol. modification. Until cheap Cl becomes available in India it is not likely that shellac will be bleached in the shellac-producing centers. F. A. WERTZ

Modern equipment in varnish manufacture. A. P. GLOECKLER. *Chem. Age* (N. Y.) **29**, 381–3(1921).—The varnish kettles of a large manufr. consist of 400-gal. jacketed kettles heated by fluid heat transmission. The circulating oil is heated by crude oil burners. The temps. of the batches are automatically recorded, and on completion of the cook, the varnish bases are run into a tank on the floor below where the necessary thinners are added during mechanical stirring. This system of cooking is adaptable to all varnishes and paint oils which are made at a temp. not above 550° F.; the increase in production above that possible with the usual coke-fired kettle is about 700%; very close temp. control is possible; fire hazard is practically eliminated; fuel cost is reduced about 20%; and labor charges are also reduced. Illus. F. A. WERTZ

A study of the oil bromide test of linseed oil. T. A. DAVIDSON. *J. Ind. Eng. Chem.* 13, 801–6, 849(1921).—Until the compn. of the linolenic glycerides has been definitely fixed, it is desirable that a detn. of insol. bromides of linseed oil be made on the oil directly instead of on the isolated fatty acids. Dissolve 4 g. of the oil in 35 cc. Et_2O; cool to 0° and add 1 cc. Br while stirring. Allow to stand for 2 hrs. and then wash the ppt. by centrifuging and decanting 3 times with 10-cc. portions of Et_2O and once with 10 cc. of EtOH. Dry at 100° for 0.5 hr. The wash Et_2O should be satd. with insol. bromides. The use of AcOH in the brominating mixt. gives low yields. For detg. Br content of the ppt., the Stepanow-Bacon EtONa method (*C. A.* 3, 873) is the most accurate. The properties and compn. of the crude oil bromide suggest that it is mainly dilinolenin-linolin bromide. Exptl. results are tabulated and given in detail. (Cf. Hehner and Mitchell, *Analyst* 23, 310(1898); *C. A.* 14, 2093, 3804.) F. A. W.

European practice in cellulose acetate and dopes during the war. PHILIP DRINKER. *J. Ind. Eng. Chem.* 13, 831–6(1921).—A brief review of the commercial development in Europe of cellulose acetate, certain of the physical and chem. characteristics required for its use in dopes, cellulose acetate solvents, diluents, thermoplastic combinations, pigmentation, camouflage, application of dopes, and recovery of solvents and cellulose acetate from discarded fabrics. A bibliography is included. F. A. WERTZ

A new apparatus for testing insulation of enameled wires. G. STRAUBEL. Siemens-Halske Lab. *Elektrotechn. Z.* 42, 1075(1921).—A convenient and rapid testing app. consisting of a Hg bath (connected to one end of a 110-volt supply) through which the enamelled wire (connected to the other terminal) is passed. A defective spot in the enamel coating gives rise to short circuit and is automatically registered on an indicator. Full particulars are given. C. G. F.

Grinding (SEAMAN) 13. Northeastern part of Labrador and New Quebec (COLEMAN) 8.

Oxidizing iron to form pigments or similar compounds. F. BALL. U. S. 1,385,769, July 26. In the production of pigments, pieces of Fe are supported in the form of a column within a body of $FeSO_4$ soln. while treated with steam and air or other oxidizing agent. The ppt. formed may be calcined.

Coating for ship screw shafts. A. FREESE. U. S. 1,385,911, July 26. See Brit. 147,611(*C. A.* 14, 3806).

Coating composition impervious to gasoline. M. I. STRAUSS. U. S. 1,386,380, Aug. 2. A compn. adapted for coating joints of storage tanks or the like to render them impervious to gasoline is formed by dissolving shellac in an alk. soln., *e. g.*, NaOH soln., pptg. with acid, *e. g.*, dil. H_2SO_4, dissolving the ppt. in alc. and mixing the soln. with pigments or fillers.

27—FATS, FATTY OILS AND SOAPS

E. SCHERUBEL

The unctuousness of fats. PAUL WOOG. *Compt. rend.* 173, 303–6(1921).—Fats possess a property, independent of viscosity, which is revealed to the touch as a sensation of gentle slipperiness. This property is at its max. in animal fats, next come the vegetable fats and then the mineral oils. W. considers unctuousness a complex phenomenon resulting from the different manifestations of the mols. The factors which det. this property are: the form, elastic rigidity, resistance of the mols. to rotation, the viscosity, surface tension and adsorption. To support this view, the mol. vol. of a no. of lubricants was detd. by cryoscopic methods. Several detns. at different

concns. were made for each lubricant and curves plotted with the figures obtained. The curves for mineral oil, castor oil and lanolin indicate that the mol. wts. decrease with decreasing concn. of the solns. For animal and vegetable oils the direction of the curves is the opposite. A table is given showing the oils arranged according to family in the order of their decreasing mol. vol. This characteristic is greatest for the fatty oils and clearly places them above mineral oils of the same viscosity.

E. S.

The quantitative separation of the lead salts of the saturated from the less unsaturated fatty acids. ARMIN SEIDENBERG. *J. Am. Chem. Soc.* **43**, 1323–36(1921); cf. *C. A.* **11**, 3453.—In order to sep. the Pb salts of satd. fatty acids from those of the unsatd. acids the salts were dissolved in 3 solvents (alc., $CHCl_3$ and Et_2O), the last 2 of which are more volatile than the first and at the same time exert a greater solvent action, and the solvents were then volatilized until all the less sol. salts were pptd. This gives sharper and more easily controlled sepns. and is more convenient and thorough than any other method. It permits a practically complete removal of all the salts of the satd. acids from their solns., including solvents used in purifying the ppts. The fractionation process was varied in different expts. but the results were in fair agreement and were independent, within wide limits, of the amts. of the fatty acids used. An attempt was made to det. the effect of the presence of unsatd. acids upon the results. From oils or fats contg. the more unsatd. acids, such as linolenic, it is not possible to obtain the satd. fatty acids in an approx. pure state by either the fractionation or the Pb salt-Et_2O method. On the other hand, the free fatty acids isolated from the main residues obtained from the oils contg. the less unsatd. acids (oleic and linolenic) were found to have practically no I no. and to be readily sol. in petr. ether. There was no evidence of the presence of any unsatd. or HO acids. It may be concluded, therefore, that in an oil or fat from which the more unsatd. acids are absent, not only can the bulk of the satd. acids be secured with a high degree of purity by the fractionation method, but also that the value obtained for the total % present may be taken as very nearly correct.

C. A. R.

The saponins and their use. A. MEYER. *Z. deut. Oel-Fett-Ind.* **41**, 536–8(1921).—A popular account of their prepn., their properties—lathering in H_2O and permanently suspending finely solids—and more in detail their uses in *cosmetic prepns.*, as foam producers in *beverages* and as substitutes for *soaps*, especially for fine fabrics and delicate colors. Mention is made of the saponin content of *cottonseed meal*, hitherto unnoticed.

Grape-seed oil. HENRI ASTRUC. *Rev. vit.* **55**, 162–70(1921).—A review of the present status of the grape-seed oil industry, methods of extn., and applications of the products.

PAUL R. DAWSON

Chemical composition of peanut oil. GEORGE S. JAMIESON, WALTER F. BAUGHMAN AND DIRK H. BRAUNS. *J. Am. Chem. Soc.* **43**, 1372–81(1921).—The 2 samples of oil used (from the white Spanish type of peanuts grown in South Carolina and from the Virginia type of peanuts grown in Virginia) had the following consts., resp.: d_{25}^{25} 0.9148, 0.9136; I no. (Hanus) 90.1, 94.8; sapon. value 188.2, 187.8; unsaponifiable matter (%) 0.22, 0.27; acid value 0.12, 0.03; Ac value 8.7, 9.50; R.-M. no. 0.27, 0.21; Polenske no. 0.12, 02.9; satd. acids (%, cor.) 20.6, 16.4; unsatd. acids (%, cor.) 74.6, 78.7; I no. of unsatd. acids 121.8, 118.2. They consisted of the glycerides of the following acids: oleic 52.9, 60.6; linolic 24.7, 21.6; palmitic, 8.2, 6.3; stearic, 6.2, 4.9; arachidic, 4.0, 3.3; lignoceric 3.1, 2.6%. Hypogaeic acid was carefully tested for but could not be detected.

CHAS. A. ROUILLER

The application of Villavecchia's test to olive oils. J. PRAX. *Ann. fals.* **14**, 270(1921).—Certain olive oils, more particularly Tunisian oils, give a red color with Villavecchia's reagent, which might be mistaken for that due to *sesame oil*. The follow-

ing procedure destroys the power of genuine olive oils to give this red color, but does not affect the power of sesame oil to give it. Ten cc. of 90% alc. contg. 10% NH_4OH are shaken vigorously with 10 cc. of oil, and the mixt. is heated 5 min. in boiling H_2O to drive off the alc. and NH_4OH. The oil thus treated does not give any red color, and the acid which seps. is yellowish white and does not change color for some time. The sensitiveness of the reaction for the detection of sesame oil is not affected, and a + reaction is obtained in the presence of 0.1% of sesame. Cf. Marcille, *C. A.* 3, 2245; 5, 732. A. P.-C.

Hexalin and methylhexalin, two new bases for special soaps. R. Hueter. Dessan. *Z. deut. Oel-Fett-Ind.* 41, 534–6(1921).—Hexalin (cyclohexanol), d_{20} 0.945, b. 160°, flash point 68°, and methylcyclohexanol (a mixt. of the 3 isomers), d_{20} 0.930, b. 170–80°, flash point 68°, are the hydrogenation products of phenol and cresol. Both have a camphor-like odor and readily dissolve fats, oils, resins, etc., even oxidized fats like linoxyn. They are but little sol. in H_2O, but soap solns. dissolve large quantities to a clear soln.; Mg and Ca soaps are dissolved in these 2 solvents and remain in soln. when a soap soln. is added, so that hard waters produce hardly any turbidity. Tetralin, turpentine, CCl_4 and mineral oils, even of higher sp. gr., are likewise sol. in soap solns. contg. these solvents and caustic alkalies saponify fats more readily when they contain hexalin or methylhexalin, especially the former. Equal parts of light colored oleic acid, hexalin and H_2O will form a satisfactory soap soln. when simply neutralized with KOH. If 25–50 parts of H_2O are added to this soln. it gelatinizes to the consistency of soft soap and again becomes clear on further addition of H_2O. Methylhexalin under these conditions gels with less H_2O and when more solvent is added clears up again, but gels again when dild. with small quantities of H_2O; very large additions of H_2O produce, as with hexalin, permanently clear solns. Other fatty acids (linseed-oil or fish-oil acids) behave like oleic acid, but the soaps from rape oil gelatinize more readily, while coconut-oil and palm-kernel oil soaps show hardly any such tendency. Na soaps form a stiffer jelly than K soaps, stable even in summer heat. Several formulas for soap charges are given, *e. g.*, (1) 500 linseed oil (parts by wt.), 250–300 hexalin, 199 50° KOH, 1208 H_2O. (2) 500 linseed-oil fatty acids, 750 methylhexalin, 208 50° KOH, 292 H_2O. (3) 200 coconut oil, 130 linseed oil, 200 hexalin, 156 50° KOH, 880 H_2O. These charges require only mixing in a steam-heated kettle until a clear soln. results which is sol. in H_2O. The resulting soaps possess extraordinary cleansing properties and are recommended for the textile industry and laundries. They lather well, less so when large amts. of solvents are present. Hard soaps of surprizing cleansing quality can be produced by adding 10–20% of the solvent to a coconut oil charge for half boiling; example: 25 tallow, 25 coconut oil, 5–10 hexalin, 25 37° NaOH. P. Escher

The modern arrangement of a soap-powder factory. Gg. Illert. *Chem. App.* 8, 133–5(1921).—I. states his purpose to be "a detailed description of the operation of a profitable soap-powder factory in such a way that even the small operator who has no consulting operating engineer can determine whether his factory is being operated according to modern methods." 6 cuts, including a sectional elevation of a plant, are given. J. H. Moore

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Reaction velocity in hydrogenations by platinum black (Vavon) 2. Critical temperatures of solution of fats in mixtures of ethyl and amyl alcohols (Vandevelde) 2. Kieselguhr for the retention of precipitates and turbidities in oil (Bruhns) 7.

Deodorizing oils. J. W. Bohman and T. M. Godfrey. U. S. 1,385,660, July 26. Oils are deodorized by bringing the oil in the form of a spray *in vacuo* into contact

with steam, H or other suitable gas or vapor at a temp. sufficiently high to effect evapn. of the odoriferous constituents of the oil, and the unevapd. oil is quickly removed to a zone of much lower temp.

Refining cacao oil. J. N. TUTTLE and J. W. PHELAN. U. S. 1,386,471, Aug. 2. Cacao oil is refined by agitating it with fuller's earth which has been treated with lime water and then filtering the oil from the fuller's earth. This treatment serves to remove the taste and odor of the oil.

Refining cacao oil. E. J. WALL. U. S. 1,386,476, Aug. 2. Cacao oil is subjected to the action of ultra-violet rays to destroy its objectionable taste and odor.

Refining cacao oil. J. W. PHELAN and E. J. WALL. U. S. 1,386,527, Aug. 2. Cacao oil or similar oil is improved in taste and odor by exposing the oil in thin layers to the action of a current of hot air for 20–30 days.

Soap. A. TRAUBE. U. S. 1,385,735, July 26. A soln. of a fatty acid in C_6H_6 is brought into contact with an alkali such as NaOH lumps in the absence of H_2O in order to form soap.

Detergent mixture. S. A. HARTMANN. U. S. 1,387,153, Aug. 9. A detergent adapted for cleaning spots from textile fabrics is formed of castile soap 1 lb., KNO_3 4 oz. and a dil. aq. soln. of NH_3.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Report on the most important articles in the field of pure sugar chemistry published during the first half of 1921. E. O. VON LIPPMANN. *Deut. Zuckerind.* **46**, 414–5, 426–7, 440–1, 455–6, 464–5, 478–9(1921). Cf. *C. A.* 15, 2009. F. W. Z.

Sugar-cane wax. J. C. N. EASTICK. *Chem. Trade J.* 69, 282(1921).—Filter-press cake from sugar-cane juice does not contain 10% of wax, as stated in *Chem. Trade J.* 69, 217. The figure given refers to dry cake, in which the wax averages 10–12%, and may be as high as 17%, in certain varieties of cane. If there is less than 10%, its commercial extn. is hardly profitable. Wax is recovered commercially in Java and in Natal on a limited scale; its purification and bleaching are difficult. Decolorizing carbons have given fair results. The wax m. 60–62°, has an acid value of 47, and a sapon. number of 177. F. W. ZERBAN

Can the refractometer be recommended for use in the laboratory of the sugar factory? A. HERZFELD. *Deut. Zuckerind.*, Special number, 32; *Arch. Suikerind.* **29**, 1038–42(1921).—In spite of its well-known advantages, the refractometer is not as generally used in sugar houses as it should be. The objection is often made that the figures for dry substance obtained by its use agree neither with the total solids by drying nor with those by spindling. However, as long as only comparative results are needed, like in the sugar house, it makes no difference which method is used, as long as it is the only one employed. The new sugar refractometers made by Zeiss and by Goerz (illustrated) are simple and accurate and can be read easily up to 95% total solids, and should certainly be found in every sugar lab. The instrument is also useful for detn. of fine grain, according to Dědek (*C. A.* 15, 187). F. W. ZERBAN

Apparent grain in molasses. N. SCHOORL. Pharm. Lab., Univ. of Utrecht. *Arch. Suikerind.* **29**, 1055–9(1921).—There is a fundamental error in Kalshoven's method of detg. fine grain in molasses (*C. A.* 14, 860, 3335), as previously suspected by Dědek (*C. A.* 15, 187). This error is, however, not due to contraction of the molasses upon dilu., but to the fact that the curve denoting the relation between concn. and refractive index is convex toward the concn. axis in the case of sugar, while it is practically

a straight line in that of salts. The error naturally increases with the ash content of the molasses. The proper way to det. fine grain is the method of Dědek. F. W. Z.

A process for producing palatable sirup from sugar beets. Sidney F. Sherwood. *J. Ind. Eng. Chem.* 13, 799–801(1921).—The beets are washed, and the tops, upper green portions, and peel removed. The beets are sliced, the slices being permitted to fall directly into warm water of sufficient depth to prevent access of air to the slices, heated to about 80° for about an hour, and the ext. is drained off. This ext. is placed in an autoclave, heated to 108° to 110° and maintained at this temp. for 1 hr. The ext. is strained and boiled directly to a sirup. The objectionable odor and flavor of beet sirup is removed, and a palatable sirup produced. Also in *Louisiana Planter* 67, 174–5 (1921). J. J. Willaman

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The influence of fertilization and spacing upon the yield and composition of sugar beets (Gerlach) 15. A revision of the optical method for analyzing mixtures of sucrose and raffinose (Browne, Gamble) 7. Apparatus for evaporating or concentrating waste waters from molasses or similar liquids (U. S. pat. 1,385,499) 1.

29—LEATHER AND GLUE

ALLEN ROGERS

Chamois leather. B. Kohnstein. *Haute und Lederberichte* No. 23(1920); *Collegium* 1921, 338–9.—The usual methods of producing chamois leather are described. Most of this leather is made from deer or chamois skins, but sheepskins and, for piano key or buffing leather, steer hides are used. Recent methods of unhairing sheepskins are by sweating, to save lime, or by a lukewarm soln. of $(NH_4)_2CO_3$ (5 g. per l.). For tanning, a strongly oxidizable fish oil is used with $CuSO_4$ as a catalyst. Some skins have lately been dyed with acid or substantive dyes after retanning with Cr. Bleaching may be by sunlight or by a 0.5% soln. of $KMnO_4$ followed by a dil. H_2O_2 soln. (100 cc. H_2O_2 and 100 cc. H_2SO_4 in 2 l. water). I. D. Clarke

Cellulose acetate in artificial leather manufacture. Maurice Deschiens. *Chem. Age* (N. Y.) 29, 370–1(1921).—Lilienfeld in 1914 first called attention to the use in artificial leather manuf. of cellulose acetate, with phenol esters, remaining liquid at 0°, as softening agents instead of the usual fats and oils. He also recommended the addition of ground leather or cork, asbestos, or kaolin as fillers and of gutta-percha or drying oils to increase pliability, but they are not used to any great extent. Cellulose acetate may be used in place of oils or fats for making waxed cloth or paper and when mixed with heavy metal oxides, it is a good material for rendering fabrics impenetrable to Röntgen rays. If a volatile catalyst is used the acetate may be applied to the fabric direct from the hydrating bath and then pptd. and freed from AcOH by running the fabric through H_2O. The plasticizer may be added to the original acetating bath. Compd. fabrics may be prepd. by forming a film of cellulose acetate on a polished surface, pressing the fabric, moistened with a solvent, onto the film and stripping from the surface. I. D. Clarke

The analogies between research on leather and fibrin. W. Moeller. *Collegium* 1921, 314–19.—Herzog and others successfully used Nägeli's micellular hypothesis in the study of leather fibers and consider this hypothesis very important. Comparison of Heuser's work on cellulose and M.'s work on leather shows that the processes of oxidation, hydrolytic decompn., and acid or alk. hydrolysis of the two materials are identical. Leather chemists must, therefore, keep in touch with and make use of the advances in the chemistry of fibrin. Röntgen rays were used by Zsigmondy in the study of gelatin gels and his results support M.'s theory of the gel structure. I. D. Clarke

Birchtar (HOLMES) 17.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

The selective cultivation of rubber. A. A. L. RUTGERS. *India-Rubber J.* **62**, 31-2(1921).—An account of what has been done to date in Sumatra in regard to improving the yields of *Hevea* trees by seed selection and by budding. G. S. W.

The mechanical properties of calendered sheet. A. VAN ROSSEM. *India-Rubber J.* **62**, 343-5(1921).—Tensile tests on calendered sheet show that the material has a much greater tensile strength and much lower ultimate elongation in the longitudinal than in the transverse direction. This difference is attributed to a state of strain arising in the following way: While passing between the first and second rolls, the rubber becomes stretched; next, while rotating with the second roll, the heat tends to bring about contraction; but, owing to adhesion to the rolls, such contraction is impossible. Heating for 2 hrs. at 70° leads to disappearance of the state of strain and of the difference in tensile properties in the longitudinal and transverse directions. A difference in tensile properties in the two directions is retained during vulcanization by the Peachey process, but is lost during hot vulcanization. Calendered gutta-percha and balata show great differences in the ultimate elongation but no differences in the tensile strength in the two directions. G. S. WHITBY

The new process of cold vulcanization of R. Bruni. A. D. LUTTRINGER. *Caoutchouc & gutta-percha* **18**, 11018-9(1921).—A description of the new process of Bruni (*Giorn. chim. ind. appl.* **3**, 197(1921)) for vulcanizing in the cold. The method is a departure from that of Parkes or of Peachey in which vulcanization takes place by virtue of the peculiarly active form of S, for it depends upon the formation of an org. accelerator within the mass of an ordinary rubber sulfur mixt. By the synthesis of the accelerator uniformly within the mass, the accelerator shows an abnormally high activity compared with that resulting from its usual method of incorporation. The accelerators concerned in the patent (English patent 140,387; *C. A.* **14**, 2278) are alkyl dithiocarbamates of bivalent and tervalent metals, notably Zn. Dealing with $(PhNH)_2CS$ specifically, 2 procedures can be employed, (1) a mixt. of rubber, ZnO and $PhNH_2$ is exposed to the action of CS_2 vapor at room temp. or (2) the same mixt. is dispersed in an inert solvent like C_6H_6 or CCl_4 and excess CS_2 is added to the soln. or suspension. By evapn. a perfectly vulcanized residue remains. $PhNH_2$ can be replaced by its homologs, such as *o*-, *m*- and *p*-$MeC_6H_4NH_2$, $Me_2C_6H_3NH_2$ or by other types of aromatic amines, like α- and β-naphthylamines, which form substituted dithioureas. The presence of a metallic oxide is essential. A mixt. cited is 100 rubber, 8 S, 20 ZnO, 6 $PhNH_2$ dispersed in 600 of C_6H_6. Addition to this of 300 of CS_2 yields at room temp. on evapn. a perfectly cured product. C. C. DAVIS

Mechanism of action of certain accelerators of vulcanization. G. BRUNI AND E. ROMANI. *India-Rubber J.* **62**, 63-6(1921).—Thiuram disulfides are capable of affecting vulcanization without the addition of free S. Thiuram disulfides may result from the action of S on metallic dithiocarbamates. Hence it is supposed that the mechanism by which alkyl and aryl dithiocarbamates, acting in the presence of S and ZnO, accelerate vulcanization involves the formation first of the Zn salt and, from that, of the thiuram disulfide; the latter is the active agent. It is supposed that Zn alkyl xanthates and Zn mercaptothiazoles act similarly, through similar disulfides. It is further supposed that the accelerating effect of a variety of other substances is indirectly referable to the activity of mercaptothiazoles. It is found that mono- and diphenylthioureas, when heated with S at 250° in sealed tubes, yield mercaptobenzo-

thiazole, and that other aryl thioureas also yield mercaptothiazoles under similar conditions. Methylene-aniline also yields mercaptobenzothiazole when heated with S. Mercaptothiazoles similarly arise from trisubstituted, but not from tetrasubstituted thioureas. This last observation is in accord with the view that a preliminary breaking-up of the thiourea with the production of a mustard oil is necessary for the formation of a mercaptothiazole under the influence of S. ZnO accelerates the formation of mercaptothiazoles in the cases mentioned above. The mercaptothiazoles differ from the xanthates and dithiocarbamates in the circumstance that, not only their salts with Zn, but also their salts with other metals, such as Cd, Pb and Hg, are very active accelerators. Also in *Giorn. chim. ind. applicata* 3, 351–4(1921). G. S. WHITBY

The new vulcanization and accelerators. I. ANDRÉ DUBOSC. *Caoutchouc & gutta-percha* **18**, 11012–5(1921).—An historical summary of the earlier theories of vulcanization, including the juxtaposition theory of Payen, the purely chem. theories of Hinzerliog and of Unger, and the elaborate physicochem. theory of Seligmann. C. C. D.

Some applications of capillary and electrocapillary chemistry (LEWIS) 2.

Purifying rubber and similar materials. C. H. GRAY. U. S. 1,386,055, Aug. 2. Rubber, gutta-percha or similar materials are freed from impurities such as sand by mechanical treatment in the form of crumb or thin sheets while exposed to the action of HF.

Regenerating waste rubber. C. GEORGI. U. S. 1,385,869, July 26. Old or waste rubber contg. fibrous material is agitated with a heated solvent under pressure in a closed vessel to ext. the rubber from the fibrous material.

Vulcanizing rubber. G BRUNI. U. S. 1,386,153, Aug. 2. Rubber is vulcanized by treating it with S and a salt of dithiocarbamic acid, *e. g.*, the salt of Mg, Zn, Cd, Hg, Fe, Cr or Sb, and heating it to a temp. of about 100° or lower. The dithiocarbamate serves to induce vulcanization at relatively low temps.